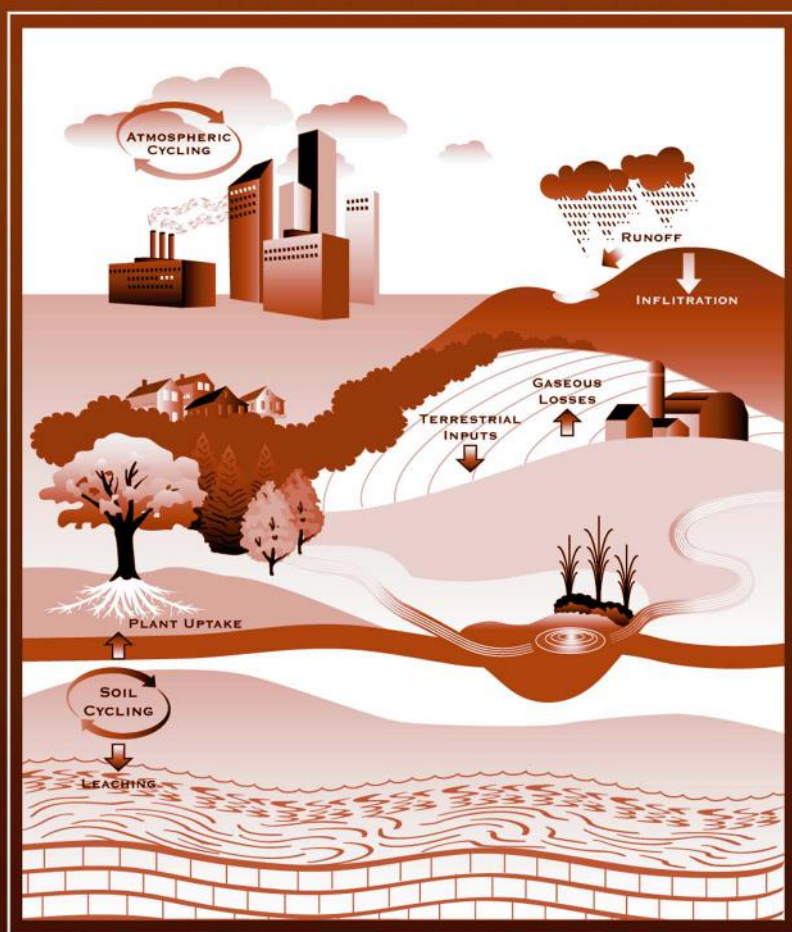


THIRD EDITION

SOILS AND ENVIRONMENTAL QUALITY



GARY M. PIERZYNSKI
J. THOMAS SIMS
GEORGE F. VANCE



Taylor & Francis
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Dedicated to the families of the authors

Joy, Garrison, and Jeanne

Connie, Amy, Ethan, and Katy

Maureen, Christy, Emily, Malaki, and Kya

whose continued love and patience made this book a reality

Preface

There are numerous reasons why people should be interested in environmental science. Obviously, we all live in, utilize, and depend upon the environment, so environmental quality should be a concern to everyone. Very little of the Earth's land surface is left in a natural state as nearly all of it is managed as urban areas, parks, recreation areas, forests, rangeland, pastures, mining operations, or cropland. People should appreciate how our use of the landscape influences the environment regardless of their occupation. Everyone is a consumer of food, which suggests we should also be familiar with the environmental costs vs. benefits of our food production practices. Environmental science is a topic without bounds and can be intellectually stimulating for the curious individual. Rarely do we find a subject that spans basic to applied research, crosses multiple disciplines, has significant interactions with social, legal, and political issues, and provides fertile ground for life-long learning.

This third edition of *Soils and Environmental Quality* explores environmental quality from the aspect of soil science, and has been updated to include current topics, relevant problems, and an increased emphasis on management. Soils play a vital role in the quality of our environment. For example, soils affect the quantity and quality of our food, support the various biomes throughout the world, serve as the foundations for our structures, and interact with the hydrosphere and atmosphere. An understanding of soil properties and processes is therefore critical to the evaluation of how many contaminants and pollutants, as well as essential nutrients, behave in the soil environment. Soils can be a source, a sink, or an interacting medium for the many contaminants and pollutants that affect humans, plants, wildlife, and other organisms.

In this book, we first provide an overview of basic soil science, hydrology, atmospheric chemistry, the classification of pollutants, and the fundamentals of soil, plant, and water analyses. Nitrogen, phosphorus, sulfur, trace elements, organic chemicals, global climate change, acid deposition, and remediation of contaminated soils and groundwater are discussed in depth. We have also included comprehensive discussions of nutrient management planning. Interactions of potential pollutants with terrestrial ecosystems and aquatic and atmospheric environments are emphasized. The concept of human and ecological risk assessment is reviewed using several contemporary examples such as pesticide concentrations in drinking water and contamination of soils by trace elements in organic by-products.

It has now been 10 years since the first edition of this book was published. As environmental science is always evolving, so too has this book. There have been substantial updating, improvements, and additions for this third edition as compared to the second edition:

- Material is extensively updated with each edition of this book. Many subjects covered in the second edition have evolved considerably since its publication. Examples include the topics of global climate change and the use of soil carbon sequestration as a possible remedy, nutrient management legislation, use of phosphorus assessment tools for predicting risk of phosphorus loss from the landscape, emerging groups of potentially harmful organic chemicals, ecological risk assessment, and methods for assessing the bioavailability of trace elements in soils.
- We continue our emphasis on case studies, which are presented as environmental issues/events boxes. We strongly encourage instructors to utilize these, as well as decision case studies found in various teaching journals (see Appendix for examples), in their teaching efforts.
- A new chapter on environmental testing of soil, plants, water, and air has been added to complement our extensive use of testing results throughout the book.
- The number of example problems within the chapters has increased. Environmental science is a very quantitative field and students requested more example problems to help with the basic concepts of unit cancellation and algebra.
- A new chapter on nutrient management planning has replaced the chapter on biogeochemical cycling. Given recent emphasis on nutrient management at the state, national, and international

levels, we felt a separate chapter on this subject was warranted. Material in the original chapter on biogeochemical cycling that did not fit into nutrient management was shifted to other chapters.

- The chapters have been reorganized into the subheadings of Fundamentals of Environmental Quality; Nutrients, Management, and Environmental Quality; Inorganic and Organic Contaminants; and Contaminant Assessment and Remediation to better place each chapter into the proper perspective.
- A section of color figures has been included. Color photographs convey certain information in a far superior manner as compared to words. Color graphics can also enhance the presentation of information relative to black and white photographs.
- Material has been reorganized based, in part, on input from readers of the first two editions. The discussion of sorption phenomena has been consolidated into a single chapter, for example, and the discussion of remediation is presented in a new, improved fashion.
- Increased reliance on the Internet has been recognized through incorporation of numerous Internet sources for a considerable amount of the information presented in the book in addition to the use of Internet sources for solving the problems presented at the end of each chapter.

This book is intended for use as a text for an upper-level undergraduate course in soil and/or environmental sciences, at a level that requires the reader to have a basic knowledge of chemistry. With appropriate supplementation, we believe this book could be used as a basis for a graduate-level course as well. Individuals with an interest in soil science, environmental engineering, forestry, environmental science, chemistry, biology, geology, and geography will also find this book useful. Instructors are strongly encouraged to incorporate discussions of environmentally related current events into their classroom activities as many of these topics are covered in this book. Current events also illustrate the political, economic, and regulatory aspects of environmental issues; demonstrate the human side of environmental problems; provide examples of the use and misuse of the scientific method; and may illustrate bias in the way information is presented. We would appreciate comments and suggestions that you, as readers of this book, feel would assist us in improving future editions. We have incorporated many such suggestions into this third edition.

Gary M. Pierzynski
J. Thomas Sims
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The Authors

Gary M. Pierzynski, Ph.D., is a professor of soil and environmental chemistry in the Department of Agronomy at Kansas State University. He received his B.S. in crop and soil sciences (1982) and his M.S. in soil environmental chemistry (1985) from Michigan State University in East Lansing. He earned his Ph.D. in soil chemistry (1989) from The Ohio State University, Columbus.



Dr. Pierzynski's research interests include trace element chemistry, remediation of trace element-contaminated soils, phosphorus bioavailability, water quality, risk assessment, and land application of by-products. He currently serves as editor of the *Journal of Environmental Quality*. Other professional activities include serving as soil and environmental division chair for the Soil Science Society of America; USDA-NRI panel manager for the Soils and Soil Biology Program; vice-chairperson for the Soil Remediation Subcommittee of the International Union of Soil Sciences; co-chair of the USDA Chemistry and Bioavailability of Waste Constituents in Soils regional research committee; peer-reviewer for EPA risk assessment efforts; member and chair of the technical and organizing committees for the International Conference on the Biogeochemistry of Trace Elements Series; and technical advisor for citizen groups in the Tri-State Mining Region. He has given more than 40 invited presentations.

Dr. Pierzynski teaches courses on environmental quality — the course outline of which served as the starting point for this book — plant nutrient sources, soil and environmental chemistry, and advanced soil chemistry. Dr. Pierzynski is a fellow of the American Society of Agronomy and the Soil Science Society of America. He has received the Outstanding Teaching and Outstanding Research Awards from Gamma Sigma Delta, and has been twice named Faculty of the Semester and received the Outstanding Academic Advisor Award from the College of Agriculture at Kansas State University.

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Dr. Sims is a fellow of the Soil Science Society of America (SSSA) and the American Society of Agronomy (ASA) and served as president of SSSA in 2004. He is the recipient of the SSSA Applied Research Award, the ASA Environmental Quality Research Award, and the Outstanding Research Award from the Northeast Branch of ASA and SSSA. He also serves as vice-chairperson of Division 4 (Role of Society in Sustaining Soils and the Environment) of the International Union of Soil Sciences. He has authored or co-authored 100 refereed publications, 25 book chapters, more than 100 technical papers and conference proceedings, 40 fact sheets and notes on soil testing and nutrient management, including the *Nutrient Management Handbook for Delaware*, and has been an invited speaker in many symposia at national and international meetings.

Dr. Sims has taught environmental soil management and advanced soil fertility (undergraduate and graduate) courses for 20 years. He conducts an active research program directed toward many of the environmental issues faced by agriculture in the rapidly urbanizing northeastern United States. His research has focused on the development of nitrogen and phosphorus management programs that maximize crop yields while minimizing the environmental impact of fertilizers and animal manures on groundwater and surface water. Other research has included the development of environmental soil tests for phosphorus and nitrogen, effects of dietary modification or chemical amendment on phosphorus availability in manures and biosolids, the use of municipal and industrial by-products (biosolids, coal fly ash, water treatment residuals) as beneficial soil amendments, and trace element fate and cycling in soils.

George F. Vance, Ph.D., is the J.E. Warren Distinguished Professor of Energy and the Environment, professor of soil and environmental science, and adjunct professor in the School of Environment and Natural Resources at the University of Wyoming. He received his B.S. degree in crop and soil sciences (1981) and his M.S. degree in soil pedology/soil organic chemistry (1985) from the Department of Crop and Soil Sciences at Michigan State University. He earned his Ph.D. degree in environmental soil chemistry (1990) from the Department of Agronomy and was a post-doctoral research scientist in the Department of Forestry, both at the University of Illinois.



Dr. Vance teaches courses in environmental quality, chemistry of the soil environment, soil biogeochemistry, and various courses in reclamation/restoration ecology. He assisted in developing the University of Wyoming environmental and natural resources program and coordinated the formation of a soil science graduate (M.S. and Ph.D.) degree, the soil science/water resource M.S. option, and the reclamation and restoration ecology minor and certificate programs. For his teaching and advising efforts, Dr. Vance has been recognized as one of the University's Outstanding Teachers, and has received several Excellence in Advising Special Recognition Awards and was the first recipient of the University of Wyoming Graduate School Distinguished Graduate Faculty Mentor Award.

Dr. Vance's research efforts have focused on natural resource issues, land-use practices, and soil and environmental chemistry that include selenium problems, reclamation/rehabilitation, hazardous organics, water quality assessment, waste utilization, pesticide and nutrient mobility/fate, forest soil processes, acid deposition, soil organic matter characterization, sorption of organic chemicals, and land-use planning utilizing GIS/LESA (land evaluation and site assessment). Dr. Vance has been a principal or co-principal investigator on 68 projects funded by federal and state agencies, university programs, and private industry. He has authored or co-authored more than 350 technical publications and presented or co-presented more than 300 presentations.

Dr. Vance has been president of the American Society of Mining and Reclamation and Western Society of Soil Science; division chair, Soil Science Society of America; chairperson, Regional Research Committees; panel member, USDA and EPA grant programs; associate editor, *Journal of Environmental Quality* and *Clays and Clay Minerals Journal*; member of the Editorial Board, *Arid Land Research and Management*; and member, Wyoming Governor's Carbon Storage/Sequestration Advisory Committee. He has been an ARCPAC Certified Professional Soil Scientist since 1992. Dr. Vance has received the American Society of Mining and Reclamation's Reclamation Researcher of the Year Award and is a fellow of the American Society of Agronomy and Soil Science Society of America.

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PART I

Fundamentals of Environmental Quality

CHAPTER 1

Introduction to Environmental Quality

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1.1 INTRODUCTION

Environmental quality is a broad topic that can span many disciplines. Engineers, geographers, architects, lawyers, business professionals, health professionals, biologists, historians, and geologists, to name a few, could all be concerned with environmental quality in one way or another. Regardless of the perspective we have on environmental quality, it is a fascinating subject. It is easy to relate environmental topics to our everyday lives and there is never a shortage of current events related to the environment. The subject is intellectually stimulating because there are endless opportunities to educate ourselves, both in depth and breadth. Politics, regulatory issues, and social issues interact with science in ways not seen in other subject areas. Numerous examples of environmental policies that are successful as well as those that are failures exist if we take an international or historical perspective. The hope is that readers of this book will improve their “environmental literacy” and be able to assess and appreciate many common environmental issues facing society today.

This book takes the perspective of a soil scientist on environmental quality. Soil scientists have a unique vantage point for evaluating environmental quality because the global cycles of many substances that are potential pollutants involve soils. Many inputs used in agricultural production (e.g., fertilizers, pesticides) can be pollutants if not managed properly. Soils in nonagricultural settings can be polluted by atmospheric deposition, by improper disposal of wastes and by-products, or by accident, as in the case of chemical spills. Soil itself can be a contaminant. Soils

also interact with the hydrologic cycle and the atmosphere by serving as a source or sink for various constituents in water or air. Ultimately, everyone is dependent on soils and their role in providing food and a clean environment in which to live.

There is a strong relationship between food production and environmental quality, and this relationship is quite different from the relationship between the production of manufactured goods and environmental quality. For example, if the production of television sets presented an unacceptable risk to the environment, then society could decide not to produce television sets anymore, while the same cannot be said for most food products. We must continue to produce food, and therefore society must take responsibility for the potentially hazardous materials used in production agriculture. Note the use of the word *society*. Ideally, all individuals should understand the basic food production processes since we are all food consumers. Included in this understanding would be the risk vs. benefit issues associated with inputs in food production processes. Fertilizer and pesticide use and the application of by-products to soils are some of the practices that can have very positive effects on food production and, at the same time, present serious threats to humans and the environment.

The work of soil scientists is not confined to agriculture, however, because soil scientists are concerned with both rural and urban issues. Many activities in society can contaminate soils and lead to environmental degradation. Mining and smelting of nonferrous metals, coal mining, production and use of petroleum products, and nuclear waste are just a few activities that affect all citizens and our soil resource. Hazardous materials are used in many industrial processes and even in our own homes. We must realize that as long as hazardous materials are stored, transported, utilized, or produced as by-products, the chance exists that there will be accidental releases into the environment. In addition, most of the major atmospheric gases associated with global climate change undergo major interactions with soils.

Soil science is a broad topic, and while we are not able to cover all aspects in this book, sufficient material is presented, along with the basics of hydrology and atmospheric science, to allow the reader to understand most environmental issues involving soils. A working knowledge of the environmental issues is critical if an individual wants to have meaningful input into decisions that affect the environment. The input can come in a variety of ways, including responding during the public comment period for new environmental legislation for planned remedial actions for Superfund sites, participating at public hearings and meetings, and even supporting candidates for public office who advocate an environmental policy that is agreeable. One goal of this book is to present facts and issues as objectively as possible and to point out how biases may influence how information is presented.

1.2 ENVIRONMENTALISM

Environmental quality may seem to be a new topic when, in fact, the current emphasis on environmental quality is a renewed interest in an old topic. Modern-day environmentalism is more than 40 years old if we consider the publication of *Silent Spring* by Rachel Carson in 1962 as the beginning of widespread environmental awareness by the general public. The U.S. Environmental Protection Agency (EPA) is more than 30 years old, as are a number of scientific journals that have the sole purpose of reporting on environmental research and the Earth Day celebration. Several factors are likely responsible for the renewed interest in environmentalism. We are becoming increasingly aware that exposure to various substances may cause human health problems ranging from death to subclinical effects such as attention deficit disorder. The natural tendency is to eliminate or reduce our exposure to substances that we suspect may adversely affect human health. We are also becoming increasingly aware of the effects of various substances on a variety of organisms in the environment, and we have become more sympathetic to these indirect effects. Overall, there is increased awareness of the impact of human activities on the world's natural

resources. Finally, our ability to detect contaminants in soil, food, water, and air has greatly improved in recent years, both in terms of the type and concentration of a contaminant that can be detected. Concentrations in the micrograms per kilogram ($\mu\text{g/kg}$) or micrograms per liter ($\mu\text{g/L}$) (parts per billion, ppb) range are routinely measured with concentrations in the nanograms per kilogram (ng/kg) or nanograms per liter (ng/L) (parts per trillion, ppt) range possible for some substances. This expanded capability allows a more accurate inventory of our environment and the influences of our activities on the environment. These factors provide both the means and the motive for maintaining public interest in the environment.

Example Problem 1.1

The use of units such as ppm, ppb, and ppt is generally discouraged in scientific writings because these unit are ambiguous. The ambiguity arises from the fact that these units can be based on mass or volume. Regardless, given the widespread use of these units, the following example problem is warranted. Demonstrate that ppm by mass and mg/kg are equivalent:

$$1 \text{ kg} = \frac{1000 \text{ mg}}{\text{g}} \times \frac{1000 \text{ g}}{\text{kg}} = 10^6 \text{ mg}$$

$$\text{So 1 mg represents } \frac{1}{1,000,000} \text{ of a kg and } 1 \text{ ppm} = 1 \text{ mg/kg}$$

For aqueous solutions with a density of 1 g/cm^3 , 1 L will have a mass of 1 kg so $1 \text{ ppm} = 1 \text{ mg/L}$. The same process can be used to demonstrate that $\text{ppb} = \mu\text{g/L} = \mu\text{g/kg}$ and $\text{ppt} = \text{ng/L} = \text{ng/kg}$.

An *environmentalist* is a person who works toward solving environmental problems, and environmentalism is an attitude by a group of individuals, perhaps all of society, that the environment takes a high priority in the decision-making process. A more philosophical approach categorizes individuals' attitudes about the environment into one of three groups: *egocentric*, in which an individual's actions are guided solely by concern for himself or herself; *homocentric*, meaning concern for the human species; and *ecocentric*, meaning an overall concern for the environment. Society as a whole and most individuals have clearly progressed slowly from egocentric attitudes toward more ecocentric attitudes.

Environmentalism has been a social movement. In *The True Believer*, Eric Hoffer (1951) identified three stages of social movements. The first stage is called *people of words* (updated to be gender neutral). In this stage the social movement is discussed and debated within a small segment of society generally described as the intellectuals. Late in the first stage, the social movement may be described in various writings. Rachel Carson was a person of words. The second stage is called *fanaticism* and is characterized by an increase in awareness by society of the movement through various attention-grabbing, often illegal, actions performed by zealous believers. Environmental fanaticism may include various means of disrupting production (e.g., vandalism) from an industry that is believed to be polluting the environment or even something as drastic as bombings or kidnapping. The final stage is called *practical people of action* or, by some, *institutionalism*. At this stage there is widespread awareness and support for the movement. Protests utilize legal means and the potential for violence decreases. Organized boycotts may be employed, for example. Committees or even agencies may be formed. Ecocentric attitudes would prevail in the context of environmentalism. Eric Hoffer (1951) summarizes the above by stating, "A movement is pioneered by men of words, materialized by fanatics, and consolidated by men of action."

Environmentalism as a whole has clearly progressed to the institutional stage with the federal EPA and comparable units of government in each state and most countries. Within

environmentalism, issues continue to arise that pass through some or all of the stages of a social movement. Recent attempts by members of environmental groups to physically block the passage of whaling ships would be an example of fanaticism. The issue of global climate change due to increases in atmospheric concentrations of greenhouse gases is late in the people of words stage with no indication of fanaticism as yet.

The protection and study of soils has been an integral part of the environmental movement. Regulations exist at both the national and state levels to protect soils from contamination. The concept of soil quality assessment is being developed by scientists and offers a conceptual and quantitative framework by which the overall impact of soil management on the “health” of the soil can be determined.

1.3 STUDYING THE ENVIRONMENT: THE SCIENTIFIC METHOD

The scientific method provides a set of rules by which the scientific community conducts investigations such that experimental design, collection of data, and the interpretation of data are done in a systematic and objective fashion. The importance of the scientific method cannot be overstated. Environmental issues can be emotionally charged because they can influence human or animal health and have significant economic impacts. Decisions or actions based on poor information can result in wasted effort, superfluous expenditures, unnecessary regulations, or needless harm to the environment.

There is no agreed-upon definition of the scientific method in the sense that the same steps are followed in every scientific investigation. There are some factors common to all investigations, however, that must be present before a particular study is acceptable to the scientific community. The scientific method can be viewed as a deductive process, that is, one that proceeds from the general to the specific. In this case, the first step is *recognition of a research question*. This can come about as a result of familiarity with a given subject and simply recognizing the next step in the discovery process. Research questions also arise when new substances are deliberately (e.g., a new pesticide) or accidentally released into the environment and their fate and transport warrant investigation. Observations also generate research questions. Environmentally relevant observations might include the discharge of a substance into the environment, a higher incidence of cancer in a community, measurement of the concentrations of a substance in an environmental media, or evidence that any organism or group of organisms is impaired in some way. Observations can be made with any of the five senses or with instrumentation; scientific instruments merely enhance the senses. A considerable amount of science is involved with making and verifying observations and much useful information comes from these measurement. Simple observations, however, do not explain mechanisms, processes, or implications; that is, what caused the observed effect or the potential harm to the environment from a particular substance.

The second step in the scientific method is the *development of a testable hypothesis*. A *hypothesis* is a plausible explanation for the observation that is tentatively accepted and may serve as a basis for further investigation. Logically, the next step in the method is testing the hypothesis. Ideally, this testing occurs through controlled experiments. *Controlled experiments* are replicated experiments in which all factors except the one in question are held constant. The replication of treatments in controlled experiments is an important point. Replications provide a means of determining if treatment effects are real (statistically significant) or due to chance (not statistically significant). The more replications that are used the more certain the investigator can be that treatment effects did or did not occur.

One observation that has been verified and is causing considerable debate is the fact that the concentrations of gases that absorb heat (radiatively active or greenhouse gases) in the atmosphere have been increasing compared with preindustrial times. Some scientists believe that the increased concentrations of radiatively active gases will cause the average temperature of the atmosphere to

increase, which will likely cause changes in the climate. Unfortunately, there is no easy-to-conduct experiment to test this hypothesis. Historical weather data provide some information, but we also know that the climate has varied considerably over time, the climate has been both warmer and colder than present conditions, and that these changes occurred without influence from human activities. Computer models can simulate the effects of increasing concentrations of radiatively active gases on the climate, but our confidence in the models is limited. Hence, the global climate change issue is stretching the limits of science and the scientific method at the moment. Some people are comfortable extrapolating the scientific facts to conclude that global climate change is already occurring, and society needs to act quickly to slow the changes, while others remain complacent, believing that science has not yet proved that there is a problem.

Other types of scientific investigations do not lend themselves to controlled experiments. Human health studies are a perfect example. Physicians may observe that patients with a certain type of cancer have been exposed to a particular chemical, but they cannot test the appropriate hypothesis with controlled experiments using human subjects. Epidemiological studies may be useful in these situations. *Epidemiology* is the study of the occurrence and nonoccurrence of disease in a population without the benefit of controlled experiments. If comparable groups (i.e., similar distributions of age, sex, etc.) that have been exposed to various levels of the chemical in question can be identified, then statistical comparisons can be conducted on the frequency of diseases between the groups. Epidemiological studies are not as good as controlled experiments and this can lead to some interesting statements. Tobacco companies have defended themselves with the argument that no one has ever conclusively proved that the use of tobacco products causes cancer. Technically they are correct because there have been no controlled experiments with humans. Health officials cite the epidemiological studies that show a strong association between tobacco use and the incidence of cancer. Individuals are left to decide which body of evidence they select to dictate their own behavior. *Clinical trials* are a mechanism for testing health effects of environmental contaminants on humans using controlled experiments. While generally used for testing new medical practices or drugs on patients, clinical trials can be used for environmental purposes under the right circumstances. The participants must be fully informed of the risks and the investigators must be reasonably certain that the effects are minimal and temporary.

Testing a hypothesis generally involves the development of a data set and a statistical analysis of that data, which the investigator must then interpret. At this point we might assume that the scientific method proceeds in a straightforward fashion. However, it is well known that different scientists may reach different conclusions from the same set of data. Real or perceived limitations in the experimental approaches used to obtain the data and variations in the application and interpretation of statistics account for some of these differences. For example, statistical tests for significance can be categorized as ranging from conservative (less likely to find a difference) to liberal (more likely to find a difference) and the presence or absence of significant effects influences the overall conclusions of a study. Most scientists are aware of these issues, can take them into account, and reach their own conclusions as needed. However, the general public is not aware and may accept an interpretation at face value. Ideally, scientists remain objective and do not let any biases influence their design of the experiment, selection of statistical approaches, or subsequent interpretation of data.

Publication of the results of scientific investigations in refereed journals is an integral part of the scientific method. If the manuscript appears in a journal then all readers are free to accept, challenge, or attempt to verify the findings. In the 1980s the prospect of cold fusion was presented publicly by two scientists. The results of an experiment were released prior to the work going through the publication process. A great deal of media and government attention was generated because of the far-reaching ramifications of cold fusion. When the details of the experiment were published, no one was able to verify the results, and the investigators and their institution suffered considerable embarrassment. Authors have a variety of journals from which to select for publication of their studies. There are clear differences in the quality of the journals, as some are highly selective

while others are less so. Those that are highly selective reject a high proportion of the submitted papers while other journals accept nearly all submitted papers. Again, it is left to the individual to place a published study in the proper perspective. For environmental topics, papers appearing in *Nature*, *Science*, *Journal of Environmental Quality*, or *Environmental Science and Technology* would be held in high regard. There are many other reputable journals as well but they are too numerous to list here.

Environmental Quality Issues/Events

Publishing the Results of a Scientific Study

The “gold standard” in science is the publication of a study in a highly regarded scientific journal. While the process varies somewhat with different journals, a generalized process for publishing a paper in a refereed journal is outlined in Figure 1.1. A manuscript must be prepared according to the style guidelines prior to submission to the editor of the journal. The manuscript is evaluated by two to three reviewers who should have the appropriate expertise and be free of conflicts of interest with the authors or the subject matter. They evaluate the work for uniqueness, adherence to the scientific method, statistical analysis, quality of writing, and overall scientific rigor. After the reviews are complete, the manuscript may be rejected for publication or returned to the authors for revisions. Generally, the reviewers and editorial board members remain anonymous when a paper is rejected. This ensures that people are free to offer their honest opinion of the work. (Scientists can get a little testy when their work is criticized!) Revised papers are further considered by the editorial board and may be reviewed again, or accepted or rejected for publication. The process is not perfect, and we would be ill-advised to believe everything that is published in refereed journals. However, given the tremendous progress that has been realized in science, it would be hard to argue that the system does not work.

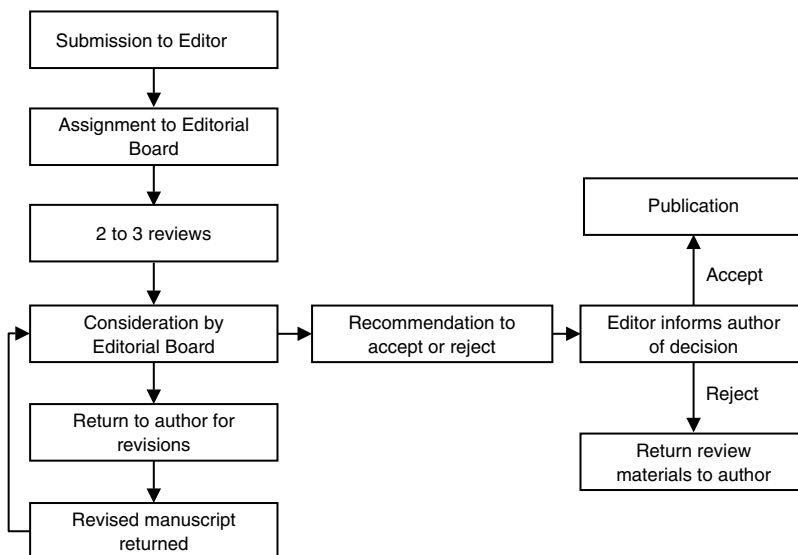


Figure 1.1 Flowchart illustrating a generalized process for publication of a scientific study in a refereed journal.

The scientific method broadly defines how we advance knowledge and there are various stages that information passes through as it moves from being unknown to being widely understood by the general public. Before an attempt is made to publish the results of a scientific investigation, all or portions of the study may be reported at a scientific meeting. These preliminary reports can be viewed as a work in progress and as a presentation that has not been subjected to the scrutiny of the peer-review process. Thus, the chance of error is much higher. Once a paper has been published in a refereed journal, the chance for errors and erroneous conclusions is reduced. If a body of literature develops around a specific topic that subject may eventually appear in textbooks, which suggests the concept is well accepted by the scientific community. The general public is exposed to the information in a variety of ways including media coverage of interesting scientific studies, our formal education system, and the vast amount of information available through libraries and the Internet.

If individuals want or need to be objective about environmental issues, they must be able to evaluate information, to recognize the source of information and whether it is a product of the scientific method. It is important to recognize information that may be biased because of vested or emotional interests. The scientific method is a useful tool for the environmental sciences because it provides a mechanism by which attainment of knowledge can proceed in an unbiased fashion and offers the best approach for removing the emotional aspects often associated with environmental issues.

1.4 ENVIRONMENTAL SCIENCE AND THE GENERAL PUBLIC

Responsibility for the environment ultimately belongs to society. Society elects the officials who promulgate the environmental regulations and who decide how tax dollars will be spent on environmental research. The responsibility is not straightforward, however, as many complicating factors exist that require extensive time and effort to evaluate before laws or regulations are legislated. Environmental regulations directly affect industries that provide jobs for society. The costs of compliance with environmental regulations by private businesses and governmental units themselves are passed on to consumers through increased prices and taxes. These interactions would tend to make for weaker environmental regulations. Countering this tendency are the fears of society about the effects of pollutants on humans and a growing respect for the environment in which we live.

Consider also the plight of countries that are not as economically well off as the United States and other economic powers. In these situations the cost of environmentally friendly practices is simply beyond reach, and the economic gains and the immediate need to produce food are given a much higher priority than environmental matters. Because many of the human health effects from environmental contamination take years to develop, it is not difficult for people to delay consideration of environmental matters in deference to more immediate concerns.

Scientific literacy of the general public and elected officials is a significant concern for environmental issues because of the breadth and depth of the science involved. Even a person with expertise in one area of environmental science may have difficulty appreciating another environmental discipline. The results of the lack of scientific literacy are varied but include an overly cautious attitude by some, to blissful ignorance by others, on the same environmental issue.

The media play a role in environmental science by transferring knowledge from the scientific community to the general public. The media report information that may be of interest to their audience provided the information comes from what the media perceive as a credible source. Careful reporting clearly identifies the status of the new information relative to the scientific method. Occasionally, stories cover the presentation of a paper at a scientific meeting, which should be viewed with more skepticism than a report that will appear in a reputable journal. Often, the general

public has difficulty placing a single media story in perspective because a synthesis of the broader picture is usually not presented. For example, numerous news stories have appeared about the possible link between exposure to pesticides and cancer. Some suggest a link exists; others cast doubt. Given the large numbers of pesticides and the many different types of cancer, it is not surprising that people are confused. In addition, some media outlets have a tendency to use sensationalism in their coverage of environmental matters.

Be aware of the difference between an environmental event and an environmental issue. An environmental event is an important occurrence related to the environment, whereas an environmental issue is a point or question related to the environment that is to be debated or resolved. A chemical spill is an environmental event, while the response to the spill, which might include actions that need to be taken to prevent additional spills, is an environmental issue. Reporting of issues and events should be objective, but objectivity is compromised most often when it comes to issues. Once again, the ability to evaluate information is the key to a complete understanding of environmental concerns.

We must also keep in mind that personal feelings about the environment involve value judgments. While individual values may vary widely, people should not expect to impose their own values onto others, and they will generally be better off respecting the values of others even when the values differ from their own. Value judgments must be taken into account even as we define pollution and contamination.

1.5 DEFINING POLLUTION AND CONTAMINATION

Before a general discussion of soils and environmental quality can be presented, a definition of the terms *pollutant* and *pollution* must be given. Interestingly, definitions of these terms will vary from individual to individual. Consulting a dictionary yields synonyms such as impure, unclean, dirty, harmful, or contaminated. Although these words are appropriate, they do not provide a working definition that is useful for studying the environment.

Part of the problem in defining pollutant or pollution is that an agreement must be reached on what constitutes acceptable use of materials that may cause pollution. For example, some would consider the use of pesticides acceptable if they are reasonably certain that the effect of the pesticide is only that which was intended, whereas others would consider the use of any pesticides unacceptable. In the first case, the pesticide is a pollutant only if undesirable side effects occur, while in the second case, the pesticide is always considered a pollutant. These are the value judgments that were discussed earlier. What constitutes an acceptable level of pollution is another way to view this problem. Attitudes will range from none (ecocentric) to any level that will not harm me (egocentric).

A second part of the problem in defining pollutant or pollution is the distinction between anthropogenic sources and natural sources. A volcano may place a greater quantity of noxious gases and particulate matter into the atmosphere than the combined output from a large number of electric power plants, but some would not consider the output from the volcano a pollutant because of its natural origin. Similarly, heavy metal mining activities may pollute soils with heavy metals, yet soils with high concentrations of heavy metals can occur naturally because of their proximity to metal ore deposits. In both examples, the environmental effects of the gases, particulate matter, and metals are the same regardless of the origin.

It should be apparent that there are value judgments associated with defining pollutant or pollution and it is impossible to change this situation. A reasonable working definition of a pollutant, taking into account the aforementioned problems, would be *a chemical or substance out of place or present at higher than normal concentrations that has adverse effects on any nontargeted organism*. The implications of this definition are that the pesticides applied to agricultural soils are not pollutants provided they do not move below the rooting zone of the crop or run off the site and affect another area. They would become pollutants if they occurred off site

at concentrations high enough to cause harm to an organism, although the possibility still exists that the pesticide will have adverse effects on nontarget organisms that live in or frequent the soil that receives the pesticide application. The volcanic output and the naturally occurring, metal-contaminated soils represent pollutants because a chemical or substance is present at higher than normal concentrations and can adversely affect living organisms. Miller (1991) states, "Any undesirable change in the characteristics of the air, water, soil and food that can adversely affect the health, survival, or activities of humans or other living organisms is called pollution," which also takes into account noise or thermal pollution in addition to pollution caused by chemicals and other substances. Both definitions allow for value judgments by using the subjective phrases "out of place" and "undesirable change."

The term *contaminated* is often used synonymously with *polluted*, although subtle differences in the definitions would indicate that these terms are not interchangeable. Contaminated implies that the concentration of a substance is higher than would naturally occur, but does not necessarily mean that the substance is causing any harm. Polluted also refers to a situation in which the concentration of a substance is higher than would naturally occur but also indicates that the substance is causing harm of some type, as noted in the two previously stated definitions. By this reasoning, a soil could be contaminated but not polluted.

The terms *toxic waste*, *hazardous waste*, or *hazardous substance* are often heard and, obviously, such materials can be pollutants. The added distinctions of toxic or hazardous are used for substances that can be acutely or chronically toxic to humans, as opposed to pollutants like sediment or phosphorus (P), which are not. There is no regulatory classification for toxic waste from a legal standpoint in most states. Hazardous waste, defined as part of the Resource Conservation and Recovery Act (RCRA), is solid waste that causes harm because of its quantity; concentration; or physical, chemical, or infectious characteristics. Harm is defined as a significant contributor to an increase in mortality or serious illness or presenting a significant hazard to humans or the environment if improperly treated, stored, transported, or disposed. When most of us think of hazardous waste, we have images of a dark, pasty substance handled by an individual in full protective gear. Most of us, however, have hazardous substances stored under our kitchen sinks in the form of drain cleaners, scouring powders, glass cleaners, and bleach.

Pollution is often broadly categorized according to its source. *Point-source pollution*, as the name implies, is pollution with a clearly identifiable point of discharge. The outflows from a wastewater treatment plant or a smokestack would be examples. *Nonpoint-source pollution* is pollution without an obvious single point of discharge. Surface runoff of a commonly used lawn herbicide or groundwater contamination from nitrate (NO_3^-) would be examples. The implications for control are quite different. Controlling nonpoint-source pollution can be difficult because of the large areas involved and the need to deal with multiple landowners and sources. One of the successes of the early versions of the Clean Water Act (CWA) was a reduction in P discharges to surface waters from numerous point sources. These sources were primarily wastewater treatment plants. Federal matching money was made available and many communities upgraded their treatment plants from primary to secondary or advanced facilities. Sensitive water bodies, such as Lake Erie and the Chesapeake Bay, benefited greatly from this legislation. However, P in surface waters remains a significant problem today. Phosphorus pollution is primarily of nonpoint-source origin such as agricultural uses of commercial fertilizers and animal manures. This contribution to the P problem will be much more difficult to solve, and is discussed in greater detail in Chapter 6.

1.6 CLASSIFYING AND CHARACTERIZING POLLUTANTS

Table 1.1 presents a broad classification scheme for pollutants based on their general characteristics or uses. Each pollutant category can affect more than one medium. Each category can represent more than one process or member. The trace elements, for example, comprise more than

Table 1.1 Classification of Potential Pollutants and Contaminants, the Impacted Media, and Primary Environmental Concerns

Pollutant or Process	Examples	Medium Impacted				Primary Environmental Symptom or Concern
		Soil	Ground		Air	
			Water	Surface		
Nutrients	N and P in commercial fertilizers, manures, biosolids, wastewater treatment effluent	*	*	*	Eutrophication, contaminated drinking water, ammonia in troposphere	
Pesticides	Insecticides, herbicides, fungicides, etc.	*	*	*	Ecological risks, contaminated drinking water, human health	
Hazardous organic chemicals	Fuels, solvents, volatile organic compounds	*	*	*	Ecological risks, contaminated drinking water, human health	
Hazardous materials	Strong acids, bases, and oxidizers	*	*	*	Acute exposure, fire hazards	
Acidification	Acid precipitation, acid mine drainage	*	*	*	Degradation of structures, ecological risk	
Salinity or sodicity	Saline or sodic irrigation water, saltwater intrusion, road salt	*	*	*	Loss of soil productivity, impaired off-site water quality	
Trace elements	Heavy metals, elements normally present at low concentrations in soils or plants	*	*	*	Human health concerns, ecological risk	
Sediments	Eroded soil in surface waters			*	Turbidity, eutrophication	
Particulates	Soot, dust from wind erosion, volcanic dusts, ash			*	Visibility, inhalation of PM ₁₀ and PM _{2.5} particles	
Greenhouse gases	Carbon dioxide, methane, and other radiatively active gases			*	Global climate change	
Smog-forming compounds	Ozone, secondary products of fuel combustion			*	Human health concerns, visibility	

20 different elements. Acidification consists of several unrelated reaction pathways, some occurring in the atmosphere and others in the lithosphere (e.g., soil), which produce acidic products that negatively affect their respective end points. Conversely, sediments are a relatively straightforward category comprised a single source.

The *nutrients* category primarily reflects the negative impacts of nitrogen (N) and P when present at high relative concentrations. Phosphorus in surface waters and NO_3^- in surface waters and groundwaters are the main indicators of environmental problems. Agricultural production practices are responsible for a fair share of the problems associated with excessive nutrients. Significant contributions are also made from private home and horticultural uses of fertilizers as well as naturally occurring sources, sewage treatment facilities, septic tanks, food-processing plants, wildlife, and livestock. From an ecological viewpoint, high nutrient concentrations in surface waters lead to *eutrophication*, the enhancement of phytoplankton growth caused by nutrient enrichment. Generally, phytoplankton are P limited in freshwater systems and N limited in marine systems. High NO_3^- concentrations in drinking water can also be a direct health threat to humans and animals.

The *pesticides* category represents a wide range of mostly organically based chemicals used to control pests such as weeds, insects, rodents, or plant pathogens. Once again, agricultural production practices account for the majority of pesticide use, with private home and horticultural uses also contributing. Pesticides are normally released intentionally into the environment at low levels, although accidental spills involving large quantities or high concentrations do occur.

Hazardous organic chemicals represent the large number of organic chemicals, other than pesticides, that are commonly used as fuels and as materials for a variety of industrial processes. These chemicals are acutely or chronically toxic to humans or other organisms when improperly administered, used, or disposed. Many of the hazardous organic chemicals have properties analogous to pesticides. However, this class of compounds is generally not intentionally released into the environment and soil contamination problems usually involve improper use, disposal, or accidental spills over small areas with high concentrations of the chemical in question. Contrast this to the environmental concerns for general-use pesticides, which generally involve applications at low concentrations to large areas as an accepted practice.

Hazardous materials include a large number of materials that generally fit the definition of hazardous waste, but are not included in the other categories. Hazardous waste was defined earlier but generally has properties that make the material harmful because it is ignitable, corrosive, reactive, or toxic.

The *acidification* category includes several unrelated processes. Acid precipitation is mainly the end result of the conversion of the oxides of N and sulfur (S) into their respective acids in the atmosphere. The concern is with precipitation having a lower-than-normal pH and its impact on the environment. Acid mine drainage represents another source of acidification where water has been acidified by the weathering and oxidation of sulfide minerals, primarily pyrite (FeS_2). Such water can have a pH as low as 2.0 and can have significant impacts on soil or surface water ecosystems. Another example is that of soils becoming acidified after heavy use of ammoniacal N fertilizers (from the nitrification process) without neutralization of the acidity with liming materials.

The primary problems associated with *salinity* and *sodicity* are reductions in plant productivity due to water stress caused by the increased osmotic potential and changes in soil physical properties (dispersion with a resultant reduction in permeability) when salt or sodium (Na) concentrations in soils become too high. Irrigation with water containing high salt concentrations and salts with a high level of Na relative to that of calcium (Ca) and magnesium (Mg) is the chief cause of these problems. Runoff from roads de-iced with sodium chloride (NaCl) onto roadside soils is another minor source of salinity and sodicity.

Trace elements are elements that are normally present in relatively low concentrations in soils or plants. They may be essential for growth and development of humans or other organisms, although many are not. Trace elements of concern as pollutants are those that cause acute or chronic

health problems in humans, animals, plants, or aquatic organisms when present above critical threshold concentrations. Examples include cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), and zinc (Zn).

Sediments represent soil particles that have eroded from the landscape and have been carried to surface waters. Areas most susceptible to erosion include construction sites, recently tilled farmland, overgrazed pastures, or clear-cut forests. Sediments can physically block light transmission through water, which can alter the ecology of the body of water; can be enriched in P; can accelerate eutrophication; and can act as sources or sinks for a variety of water pollutants. Sediments can also accumulate in surface waters, which can inhibit navigation and recreational activities and reduce the longevity of dam structures.

Particulates, *greenhouse gases*, and *smog-forming compounds* are air pollutants. Particulates are relatively inert particles generally consisting of carbon (C), soil, volcanic ash, etc. suspended in the atmosphere. Of greatest concern are particulates with dimensions of <10 or <2.5 microns (μm), PM_{10} and $\text{PM}_{2.5}$, respectively. Such particles can move deep into lung tissue through normal respiration. Greenhouse gases are the gases responsible for the greenhouse effect. The greenhouse effect is the absorption of radiated heat by atmospheric constituents that provides warming of the lower atmosphere and the Earth's surface. Humans influence the concentration of various greenhouse gases in the atmosphere — primarily carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbons (CFCs) — which makes it more difficult for radiated heat to escape the atmosphere and results in an increase in the mean global temperature above that which would occur without the human influence. Some greenhouse gases are anthropogenic and others are naturally occurring, although their concentrations are increasing in the atmosphere due to human activities. Certain aspects of food production may also increase the concentrations of some greenhouse gases. Smog-forming compounds are the ingredients for the complex process of smog production.

Two important characteristics of pollutants in the environment are *persistence* and *residence time*. Persistence refers to the length of time a given pollutant remains unmodified while present in the soil, water, or air. Basically, this refers to the resistance of a substance to be broken down into less complex substances by abiotic or biotic processes and is sometimes quantified by a half-life term. Substances that are readily broken down have a low persistence, and vice versa. Residence time is the length of time it takes a pollutant to move from one compartment to another in the environment. Example compartments would be the atmosphere, soil, groundwater, surface water, or any other location that can be defined and studied.

Persistence and residence time play major roles in pollution management and control. *Persistence* refers to the tendency of a substance to degrade in the environment, whereas *residence time* refers to the length of time a substance remains in a particular environmental compartment (e.g., the soil environment or the atmosphere). For example, organic chemicals that are halogenated, e.g., chlorine (Cl), fluorine (F), bromine (Br), are much less likely to be decomposed by microorganisms and therefore will have a greater persistence in the environment compared with nonhalogenated organic chemicals. This has led pesticide manufacturers to design nonhalogenated pesticides, as opposed to compounds like dichlorodiphenyltrichloroethane (DDT) that have very long persistence times. We know that soils have varying capacities for sorption of both inorganic and organic substances. *Sorption* refers to the tendency of soils to retain substances. Those substances that are not readily sorbed by soil or rapidly degraded will have a short residence time in the soil and will likely become groundwater contaminants, while substances that are readily sorbed by soils and that are not rapidly degraded will have a long residence time and will be lost from the soil system primarily by soil erosion. Elements, of course, cannot be broken down into simpler entities and will be persistent regardless of residence time. Efforts to address acid precipitation by controlling the release of S and N oxides to the atmosphere have been successful because of the relatively short residence times for these substances in the atmosphere.

Nutrients, trace elements, pesticides, hazardous organic chemicals, acidification, and greenhouse gases are discussed in more detail in individual chapters. Soils play a key role in the biogeochemical cycling of these materials or processes. The topics of sediments, particulates, salinity, and smog-forming compounds are only briefly discussed in subsequent chapters.

1.7 HUMAN EXPOSURE TO SOIL CONTAMINANTS

In addition to the technical aspects involved in studying the relationship of soils to environmental quality, a topic of increasing importance is that of *risk assessment*. *Risk* is the chance of injury, loss, or damage. In the context of environmental science, risk assessment is the process used to estimate quantitatively the risks associated with exposure of any organism to various substances in the environment. Risk assessment can provide the basis for environmental regulations, although the information can be ignored if society chooses to do so.

Figure 1.2 presents a schematic of the pathways for human exposure to contaminants in soils. While the thrust of this book is not entirely on the human receptor, this figure focuses the discussion for the remainder of the book by identifying the key interactions between soils and organisms. Comparable diagrams could be produced for any organism.

The major component of Figure 1.2 is the human food chain, where crops are consumed directly by people or fed to livestock and the animal products are then used by people as a food source. However, many different exposure pathways are also illustrated including direct ingestion of soil, inhalation of dust, and ingestion of contaminated water. Contaminants can be applied to soils, enter water supplies directly, or fall directly on or be directly absorbed by vegetation. Once in the soil, contaminants can leach and move to groundwater or be lost from the soil surface with runoff and enter surface waters. These water resources can be used to irrigate soils, for livestock, or as a source of water for human consumption. Soil itself can be ingested directly by humans or animals or be drawn directly into the lungs as dust (PM_{10} and $PM_{2.5}$). Children exhibit a significant amount of hand-to-mouth activity at certain ages and can consume considerable quantities of soil or indirectly consume soil through house dust. A small percentage of children exhibit pica behavior (having an abnormal craving to eat nonfood items, especially soil or paint chips) and environmental regulations written to protect these children will need to be much more stringent compared with regulations written to protect against typical soil ingestion rates.

It is necessary to differentiate the various steps a contaminant goes through as it progresses from the soil through the food chain to the human receptor. As a contaminant is transferred from one compartment to another, various processes can influence the amount that will eventually reach the human end point. As was discussed earlier, soils will sorb some substances strongly while exhibiting little sorption for other substances. Substances that do not adsorb strongly to soils will generally be more available for plant uptake, which will occur if the plant has a mechanism for moving that substance into the plant. For example, regulations pertaining to maximum permissible concentrations of Pb and Cd in soils allow much higher concentrations

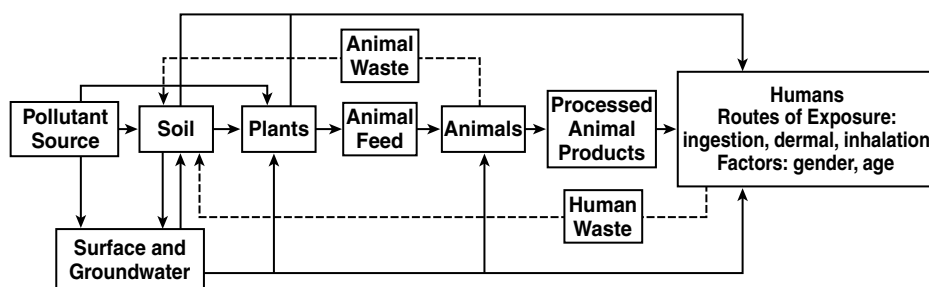


Figure 1.2 Pathways for human exposure to pollutants applied to soils. (Adapted from Brams et al., 1989.)

of Pb than Cd even though Pb is much more toxic to humans than Cd. This is because, at equal concentrations of soil Pb and Cd, Pb concentrations in plants will be much lower than Cd and, consequently, food chain transfer of Pb will be less. Similarly, contaminants can be partitioned into different body parts within an animal. Fat, organ meats, and muscle tissue will have much different concentrations of a particular contaminant. Polychlorinated biphenyls (PCBs), for example, are fat soluble and strongly partition into fatty tissue as compared with muscle tissue. Some investigators use transfer coefficients to describe the change in contaminant concentration as it is transferred from soil to plant, plant to animal feed, etc. Obviously each contaminant would require a unique set of transfer coefficients, which can have values ranging from 0 to 1000 or even higher. This approach is commonly used in risk assessments where the potential for food chain transfer of contaminants is a concern.

Figure 1.2 also depicts the recycling of human and animal wastes through soils, primarily as municipal biosolids (i.e., sewage sludge) and animal manures. This recycling usually occurs as a land application of the residual materials and is an opportunity to recycle plant nutrients and to improve the soil through the addition of organic C, but also must be managed properly to avoid overapplication of nutrients and inadvertent application of excessive amounts of contaminants. Biosolids are produced from the treatment of wastewater that may contain industrial inputs as well as human waste, thus creating the potential for contaminants to enter the soil system. Similarly, livestock are often fed or given supplements in addition to locally produced feed, which creates the potential for external inputs to enter the soil system. Scientists generally believe that land application of biosolids and manures offers far more advantages than disadvantages and the risk from contamination is negligible when managed properly. However, recent action by the U.S. Department of Agriculture (USDA) declaring that crops grown on biosolid-amended soils could not be certified as “organically grown” represented a concession to special-interest groups that were concerned about this issue.

In addition, Figure 1.2 also provides an opportunity to introduce the concept of bioavailability. A general definition is that the bioavailability of a substance is related to the possibility of it causing an effect, positive or negative, on an organism. A general example would be a therapeutic drug administered to patients in different forms, say, as a capsule compared with a tablet. If absorption of the drug by the patient (the organism and the effect) was greater for one form compared to the other at equivalent doses, we would say that the bioavailability of that form was greater. For soils we can define bioavailability as the fraction of the total amount of a substance in a soil that can cause an effect, positive or negative, on an organism. We know that at equal concentrations some substances are more likely to cause an effect than others, and for a given substance the likelihood of an effect will vary depending on the soil containing the substance. In our previous example of plant uptake of Pb and Cd, we would say that the bioavailability of Cd to plants is much greater than Pb, as shown in Figure 1.3. Further, we know that two soils with the same concentration of a given substance can produce different effects on an organism. The example illustrated in Figure 1.3 is comparable with the previous general example used for bioavailability; that is, the ingestion of equivalent amounts of a substance will produce differing effects. In this case the same amount of Pb present in two different soils produces differing blood Pb concentrations in the child after accidental ingestion by hand-to-mouth activity. The bioavailability of Pb in soils is an important parameter in communities with Pb-contaminated soils where exposure to children has significant health ramifications. The bioavailability concept can be applied in many of the intercompartmental transfers shown in Figure 1.2. We have already illustrated the soil-to-plant transfer and the direct ingestion of soil transfer.

Figure 1.2 and the concept of bioavailability can be used as a starting point for a discussion of *remediation* of contaminated soils. Knowing both the characteristics of the soil and the contaminant, we can determine where the contaminant is likely to move next (surface water, groundwater, air), whether movement through part or all of the food chain is likely, or whether direct contact with the soil is necessary for exposure to humans or other organisms. *Soil removal*, a commonly employed remediation technology, obviously eliminates all transfer of the contaminant from the soil to any other

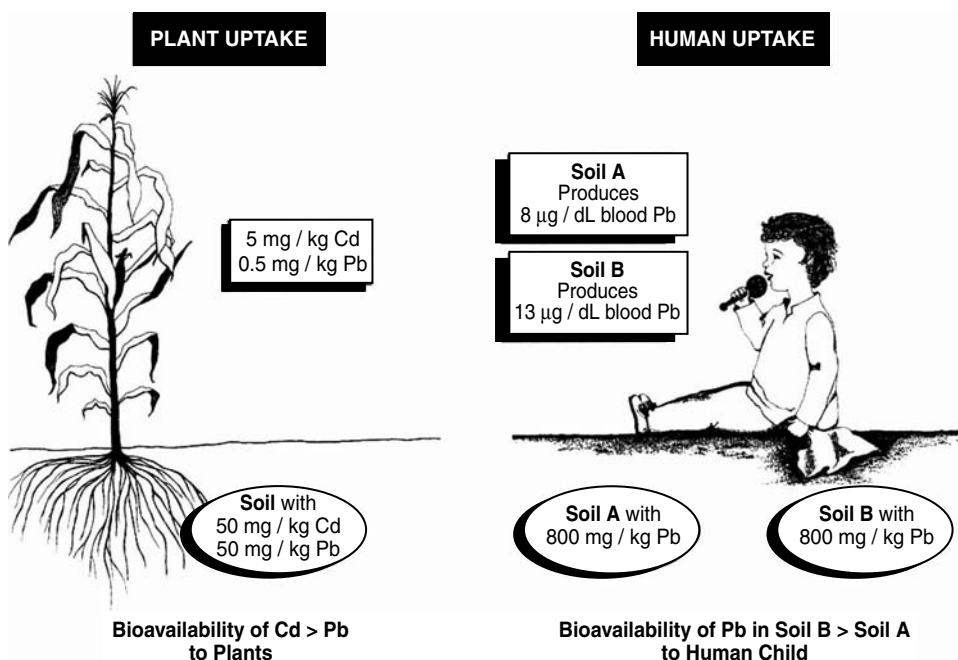


Figure 1.3 The bioavailability concept for soil contaminants. Two different trace elements can have different bioavailabilities in the same soil, and the same trace element can have different bioavailabilities in two different soils. (Drawing by Sarah Blair.)

compartment. *In situ* stabilization does not remove the contaminant from the soil but changes the form and bioavailability of the substance such that transfer to another compartment is unlikely, and can even reduce uptake of the contaminant by an organism if that soil is ingested. Vegetation can have a variety of effects depending on the identity of the contaminant. For metal-contaminated sites that did not previously have vegetation, establishment of vegetation (vegetative remediation or phytostabilization) will reduce runoff losses of soil and wind erosion, thus reducing exposure of aquatic ecosystems to metals and reducing the risk for humans from inhalation of dust. For soils contaminated with organic chemicals, vegetation can promote the biological decomposition of the substance and even promote volatilization (phytoremediation). These topics are developed in more detail in Chapter 12.

1.8 FEDERAL ENVIRONMENTAL LEGISLATION

Numerous significant pieces of federal environmental legislation have served to protect our food, air, and water; ensured prudent use of pesticides; governed the handling of hazardous waste; and provided a mechanism for cleaning up contaminated sites. Some may argue that environmental regulations are overly strict and may be an economic burden, and this may be true in some cases. However, it is clear that some environmental legislation has been tremendously successful in improving human health and the quality of our environment. Relevant examples include efforts to reduce water pollution such that the Great Lakes and Chesapeake Bay have rebounded from conditions found 20 to 30 years ago, legislation that has reduced Pb exposure for people, restrictions placed on the use of some pesticides (e.g., DDT) that have been instrumental in recent increases in the populations of predatory birds, and efforts to decrease emissions from automobiles and industry that have improved air quality. Some of this legislation is outlined in Table 1.2. The original year of enactment is given, although most legislation in this table has been updated or amended several times.

Table 1.2 Significant Federal Environmental Legislation in the United States

Federal Regulation	Year Originally Enacted	Description
Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	1947	Regulates labeling of pesticides; requires that pesticides have benefits to society that outweigh potential harm to the environment
Clean Water Act (CWA)	1948	Controls discharges into navigable waters; provides NPDES permits and TMDLs; primary authority for water pollution control programs
Clean Air Act (CAA)	1970	Established national ambient air quality standards to protect human health; has forced automobile manufacturers to reduce auto emissions; addresses acid precipitation issues and power plant emissions
National Environmental Policy Act (NEPA)	1970	Provides national policy to try to prevent or reduce damage to the environment; forces federal agencies to assess potential environmental impacts of major programs, including federally funded local programs and research
Safe Drinking Water Act (SDWA)	1974	Regulates drinking water quality in public systems; provides MCLs as water quality standards
Resource Conservation and Recovery Act (RCRA)	1976	Defines hazardous waste; forces companies to be accountable for hazardous waste from “cradle to grave”
Toxic Substances Control Act (TSCA)	1976	Allows for toxic substances control program by the EPA; controls labeling and disposal of PCBs and inspection and removal of asbestos
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)	1980	Provides authority to respond to releases of hazardous waste; provides funds for cleanup of contaminated sites that pose an imminent threat to human health; makes property owners liable for cleaning up hazardous wastes; the original Superfund law
Superfund Amendments and Reauthorization Act (SARA)	1986	Continuation of CERCLA and Superfund process; includes emergency release and other notification requirements and community right-to-know provisions
National Sewage Sludge Rule (Part 503)	1993	Describes management practices for land application of biosolids; defines pollutant limits for land application; provides limits on the amount of nitrogen that can be applied with biosolids
Food Quality Protection Act (FQPA)	1996	Modifies FIFRA and Food, Drug, and Cosmetic Act; eliminates Delaney Clause for processed foods; facilitates labeling of minor use and reduced risk pesticides, promotes integrated pest management techniques
USDA Code 590 Practice Standards	1999	Provides national nutrient management guidelines for production agriculture, including land application of animal manures
Concentrated Animal Feeding Operations (CAFOs)	2003	Defines CAFOs and requires permit for operation; requires nutrient management planning

The *Federal Insecticide, Fungicide, and Rodenticide Act* (FIFRA) regulates the labeling of pesticides, where the label is a legal document that describes the appropriate use of a particular pesticide. The labeling process forces companies to conduct required environmental testing of pesticides to demonstrate that the compound has benefits to society that outweigh any potential risks.

The *Clean Water Act* (CWA) works to ensure the integrity of surface waters throughout the United States. Two enforcement tools available to the EPA through the CWA are the national pollution discharge elimination system (NPDES) permits and the total maximum daily loading (TMDL) limits that can be imposed on a body of water. The NPDES permits control discharges from point sources of contaminants and must be renewed periodically. The EPA can shut down operations that are not in compliance with the permit or change the conditions of the permit through the renewal process. The TMDL process establishes a maximum allowable loading for a particular contaminant in a body of water and then works with all point and nonpoint sources of that contaminant to ensure that the TMDL is not exceeded.

One of the major accomplishments of the *Clean Air Act* (CAA) has been to reduce emissions of carbon monoxide (CO), hydrocarbons, and nitrogen oxide (NO) from vehicles, which has greatly improved air quality in urban areas. In addition, the act has been used to reduce emissions of sulfur dioxide (SO₂) and NO from coal-fired power plants, thereby reducing acid precipitation problems.

The *National Environmental Policy Act* (NEPA) was instrumental in creating a policy for the federal government dictating that it would act to prevent or reduce damage to the environment. Any actions by the federal government were subject to NEPA, including federally funded research grants.

The *Safe Drinking Water Act* (SDWA) regulates water treated by public water systems and uses the maximum contaminant levels (MCLs) to ensure that the concentrations of contaminants do not exceed critical values. The *Resource Conservation and Recovery Act* (RCRA) defines hazardous waste and the harm that it may cause. It also forces companies to be responsible for hazardous wastes from their creation to their ultimate disposal, the cradle-to-grave concept. The *Toxic Substances Control Act* (TSCA) created a toxic substances control program with the EPA that was essentially a reporting mechanism that creates a toxic substances inventory. Substances not regulated by FIFRA or the *Food, Drug, and Cosmetic Act* (FDCA) are covered under TSCA. The TSCA provides specific controls for PCBs and asbestos and dictates that any new substance is considered hazardous until proven otherwise.

The *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) and the *Superfund Amendments and Reauthorization Act* (SARA) represent what is commonly known as the Superfund program. This program created the *National Priorities List* (NPL), covering sites in the United States that need remediation. If those sites present an imminent threat to human health, the program has funds available for remediation. This legislation also assigns liability for cleanup costs to the generator of the hazardous waste and to current landowners. One cannot escape the cost of remediation by selling the property and one can buy into liability by purchasing property. The latter characteristic has forced prospective buyers of property to conduct environmental audits to ensure they are not buying into a large cleanup expense. This has also inhibited the sale of older industrial properties and led to the brownfields issue, or abandoned industrial properties that prospective buyers are afraid to purchase because of potential liability. The EPA has recently begun to address this issue by waiving liability so that the brownfield sites are developed for new industries rather than remaining unused.

The *National Sewage Sludge Rule* (commonly called the Part 503 regulations) provides regulations for the land application of biosolids (i.e., sewage sludge), including limits on the amounts of some trace elements that can be applied to a given site and restricting annual applications to the amount of N expected to be used for crop production. The Part 503 regulations provided the first comprehensive risk assessment of pollutants applied to soils and remain the standard by which many risk assessments are compared.

More recently, the *Food Quality Protection Act* (FQPA) has made significant modifications to FIFRA and FDCA. The FQPA now specifically promotes integrated pest management techniques, as an attempt to reduce pesticide use, and facilitates labeling of minor-use and reduced-risk pesticides. The FQPA also eliminated the Delaney clause, an absolute risk standard, for processed foods. The Delaney clause stated that pesticide residues were simply not allowed in processed foods if those pesticides were thought to be carcinogenic. While the logic of this seems sound, the requirement was difficult for the food processors to meet because pesticides are routinely used in food production and toxicology did not support the need for such a strict standard. The Delaney clause was replaced with a negligible risk standard that allows low levels of pesticide residues, similar to the way that raw foods are regulated.

In 1999, the USDA and the EPA joined forces to address the issue of *Concentrated Animal Feeding Operations* (CAFOs) and the potential environmental effects from them. The results were national standards for nutrient management from the USDA and national regulations for CAFOs from the EPA. Part of the justification for these two pieces of legislation was the change in livestock production from smaller, more widely distributed operations to fewer and larger feeding operations. Regulations by individual states were highly variable and often not sufficiently protective of the environment. Now all states must meet minimum federal requirements. The CAFO regulations provide a definition for animal feeding operations such that these facilities must obtain a permit for operation. Part of the permit involves nutrient management planning such that the application of N and P through animal manures will not exceed anticipated crop needs.

We can trace the change in public attitudes about the environment through the evolution of the environmental legislation. Prior to the publication of *Silent Spring* in 1962 by Rachel Carson there was little widespread appreciation for the potential environmental impact of pesticides or other toxic substances. The resulting increase in public awareness led to the passage of some major legislation in the 1970s. This decade produced NEPA, the CAA, a significant amendment to the CWA in 1972, RCRA, and TSCA. All of these were instrumental and tremendously successful in reducing the amount of pollutants that were released into the environment. In most areas, water and air quality are better now than they were 20 to 30 years ago, and management of hazardous substances is strictly controlled because of these important pieces of environmental legislation. The next step was the passage of CERCLA and SARA in the 1980s, which addressed cleaning up contamination that had already occurred. The passage of the FQPA and CAFO regulations indicates that we are willing to revisit environmental legislation and make needed changes. There will always be disagreements on how strict environmental legislation should be, but there is little doubt that the legislation that has been implemented has already resulted in very positive impacts to our environment.

1.9 MAJOR ENVIRONMENTAL ISSUES IN SOIL SCIENCE: A SUMMARY

An underlying theme in this book is *soil quality*, a concept that is still being developed by soil scientists and that is described in more detail in Chapter 3. The Soil Science Society of America uses the following definition:

The capacity of a specific kind of soil to function within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water quality, and support human health and habitation.

Soil functions are related to the ability of a soil to produce quality food, fiber, or feed; construction properties and limitations; the ability to support habitation and recreation; and the ability to maintain an ecosystem or desired land use. The ability of a soil to produce quality food, fiber,

or feed refers to contributions of soil to the capability of a site for profitable crop production free of harmful substances. Construction properties and limitations, topics beyond the scope of this book, refer primarily to chemical and mineralogical characteristics that influence soil properties such as shrink–swell capacity and corrosiveness that, in turn, determine suitability for basements or buried materials. Supporting habitation and recreation implies that one can have soils around homes, schools, and parks without concern for negative effects from contamination. The ability to maintain an ecosystem or desired land use recognizes the role of soils in development and maintenance of ecosystems such as a tropical rain forest. When these soils are changed, say, by exposing the soil to erosion and oxidation of organic matter by clearing the rain forest for crop or lumber production, they may lose their ability to maintain the tropical rain forest and we would note that the soil quality had been reduced. Similarly, if poor-quality irrigation water is used and soils become saline, they can no longer maintain a desired land use of crop production.

The quantification of soil quality is a difficult task at best. In the broadest sense, physical, chemical, and biological properties of a soil determine its quality. Physical properties such as bulk density and texture influence aeration, permeability, infiltration capacity, water-holding capacity, or constructive properties and can be quantified and related to quality. Chemical properties are the concentrations of organic and inorganic constituents that determine characteristics such as soil fertility, degree of contamination, salinity, corrosiveness, or shrink–swell potential and are also quantifiable and related to soil quality. Indeed, much of this book discusses the impact of excessive concentrations of nutrients, pesticides, hazardous substances, or trace elements on the function of soils. The biological component has multiple interactions with the chemical and physical aspects. Favorable chemical and physical characteristics allow for robust plant and microbial growth, which further improves chemical and physical characteristics. Thus, biological properties serve both as an indicator of soil quality and as a contributor to soil quality.

Much of the work in the soil quality area has focused on the crop production aspects of soil functions, but the assessment of soil quality relative to contamination has not been developed very much. Soil quality assessments are relative and it is easy to see how a change in soil properties, such as increasing contaminant concentrations, would be taken as a reduction in soil quality.

A very long list of individual environmental problems related to soil science could be assembled. The list would include such problems as leaking underground storage tanks (LUSTs), trace element–contaminated soils, saline soils, eroded soils, and acidified soils. It is probably more instructive to present categories of the major environmental issues in soil science. Most of the issues fall into one or more of the following categories:

1. *Reductions in soil quality because of unacceptable concentrations of pollutants.* This category includes soils that either directly or through food chain transfer expose humans or other organisms to pollutants that may cause direct detrimental effects. This category is quite extensive and includes problems associated with the pesticides, hazardous substances, and trace elements pollutant categories listed in Table 1.1.
2. *Reductions in soil quality that limit soil function.* Eroded, acidified, salt-affected, or otherwise degraded soils that can no longer support basic soil microbiological processes, a desired land use, or ecosystem fall into this category. Direct detrimental effects to humans or other organisms due to exposure to pollutants are generally not an issue in this case.
3. *Soils as a source of contaminants.* This category includes leaching and runoff losses of various chemicals or materials from the landscape. Here, the presence of a substance in the soil is not the primary problem but rather the effects of the substance on the environment as it leaves the original point of application. Thus, a reduction in soil quality as indicated by chemical analysis is not necessarily the issue but rather a conflict between soil function or use and the surrounding environment. Horticultural and agricultural uses of pesticides and nutrients would be good examples. Solving these problems ultimately requires an understanding of all risks and a prioritization of land uses and the desired quality of the environment.

Societal responses to environmental soil science issues are varied. Regulations are written that prevent soil contamination or that control the use of substances that are considered pollutants. Research is conducted on methods for remediating contaminated soils and on understanding the fate and transport of contaminants in the environment. Government programs are used to prevent degradation of soil quality by erosion. Still, considerable work needs to be completed with regard to understanding the interaction of the soil environment with potential pollutants and on utilizing the soil resource for the benefit of society while maintaining or improving environmental quality.

As we study environmental science, part of the task is familiarizing ourselves with the technical aspects, such as the scientific method, nomenclature, and processes, and another part of the task is appreciating the objectivity, philosophical approaches, and even moral questions required to have a complete understanding of environmental issues. Soils play a major role in the cycling of many environmental contaminants, and soil science serves as a useful discipline from which to study the environment. To do so we must have a basic understanding of soils, hydrology, and the atmosphere, which this book attempts to provide. The major classes of soil pollutants are then identified, followed by a detailed discussion of each. Remediation and risk assessment, as related to soils and waters, are the topics of the final two chapters.

PROBLEMS

- 1.1 List and describe the steps in the scientific method. How does epidemiology fit in with the traditional approach to experimentation?
- 1.2 Discuss how knowledge gained through the scientific method is vital to our understanding of the environment. How does the scientific method interact with the willingness of society to pass environmental legislation and to spend public resources to remediate contaminated sites?
- 1.3 Discuss environmentalism as a social movement. What are the stages of a social movement and what stage or stages are evident for environmentalism?
- 1.4 Describe the difference between an environmental issue and an environmental event.
- 1.5 Describe ecocentric, homocentric, and egocentric attitudes regarding the environment. Which type best describes your attitude toward the environment?
- 1.6 Discuss several definitions of pollutant or pollution. Which do you prefer and why? How do value judgments affect our definition of pollution? Write your own definition of pollution.
- 1.7 What is the difference between soil or water that is contaminated vs. that which is polluted?
- 1.8 Describe the various pollutant categories and give examples of each. Which involve the soil resource in some way?
- 1.9 Define bioavailability and discuss why the bioavailability of soil contaminants is important in our study of environmental quality.
- 1.10 Which pieces of federal legislation resulted in major reductions in the amount of pollutants released in the environment in the United States and started the trend of improving environmental conditions that continues today?
- 1.11 Devise a simple scheme to quantify soil quality, including taking into account the presence of contaminants.
- 1.12 Describe the major environmental issues in soil science.

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CHAPTER 2

Our Environment: Atmosphere and Hydrosphere

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2.1 INTRODUCTION

Our environment comprises natural wonders that provide for the ingredients of life, including oxygen (O₂), water (H₂O), and nutrients, e.g., nitrogen (N), phosphorus (P), and sulfur (S). Our fundamental needs are met through the air we breathe, the fluids we drink, and the foods we eat. The atmosphere contains gases such as O₂, carbon dioxide (CO₂), and nitrogen (N₂) that are essential to sustain our existence. The water we drink comes from both groundwater and surface water supplies, both of which have been cycling for millions of years. Production of plant products for human and animal consumption relies on our ability to plow, seed, and cultivate our lands. Plants require CO₂, H₂O, and nutrients, suggesting there is a need to understand how the atmosphere, hydrosphere, and soil environments sustain plant growth and support animal and human life. Environmental quality is also important in order for humans to manage natural resources sustainably, including those essential for human, animal, and other organism survival (Chiras, 2001).

The part of the planet that supports living organisms is described as the biosphere. Thus, the *biosphere* comprises all life-forms and their general surroundings, which include most hydrosphere and soil ecosystems (see Chapter 3 for more details of the soil environment). Our atmosphere is primarily composed of nonliving substances and is therefore not considered part of the biosphere. However, the atmosphere, as well as most surficial environments, influences the ecology of nearly all terrestrial and aquatic ecosystems. Biosphere impacts, both positive and negative, are often the result of lifestyles that rely on natural resource utilization that, in turn, can affect the quality of our atmosphere and hydrosphere. This chapter reviews the basic characteristics of both the atmosphere and the hydrosphere, and examines how these two spheres are important for human subsistence as well as their relationship with environmental quality.

2.2 ATMOSPHERE

We live in a time when concern for *air quality* is growing due to increasing amounts of pollutants that are added to the atmosphere daily. Our current atmosphere provides us with protection against harmful solar and cosmic radiation, moderates surface temperatures, and is a major component of the hydrologic cycle. The atmosphere also plays an important role in nutrient and contaminant transport processes. The study of the atmosphere and its phenomena is called *meteorology* and involves interactions between the atmosphere and the Earth's land and ocean surfaces, as well as various influences on living systems (Aguado and Burt, 2004; Lutgens and Tarbuck, 2004).

The atmosphere can be conveniently divided into layers separated by boundary regions, with its properties characterized by pressure and density, temperature and heat, wind circulation and patterns, chemical composition and reactions, moisture and precipitation, and atmospheric pollution. Although each of these subject areas is important to the understanding of our atmosphere, we only briefly discuss some of these topics. Understanding the interactions and processes that regulate climatic conditions is essential to developing an appreciation for how our atmosphere functions within the global environment. For more information on the atmosphere, there are several sources listed in the References and Supplementary Materials located at the end of this chapter.

2.2.1 Atmospheric Layers and Their Properties

The atmosphere consists of several layers (i.e., *troposphere*, *stratosphere*, *mesosphere*, *thermosphere*, and *exosphere*), separated by transitional zones (i.e., *tropopause*, *stratopause*, and *mesopause*), each of which has distinct properties (Figure 2.1). Of the major layers, only the troposphere and stratosphere, which comprise the *lower atmosphere* (0 to 50 km), are generally considered of great significance to humans (Ahrens, 1994). This is because the troposphere is involved in many biogeochemical processes and is the layer in which essentially all *weather phenomena* occur,

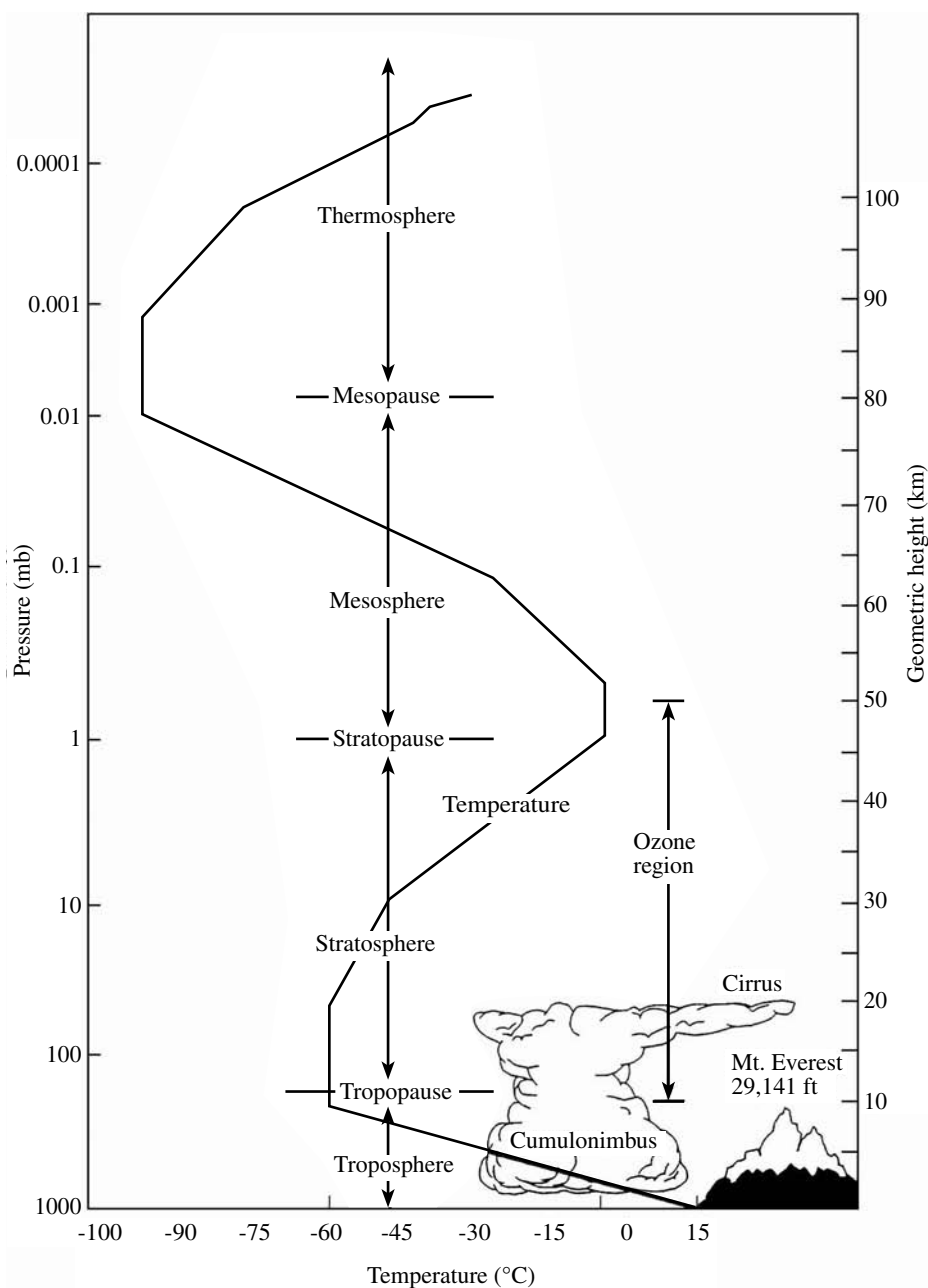


Figure 2.1 Variation in pressure and temperature in atmospheric zones to an altitude of 100 km. (Modified from Schlesinger, W. H., *Biogeochemistry: An Analysis of Global Change*, 2nd ed., Academic Press, San Diego, 1997. With permission.)

whereas the stratosphere contains the ozone (O_3) layer that protects the Earth's surface from harmful ultraviolet (UV) radiation. The atmosphere becomes more and more tenuous with increasing height, eventually tailing off into the interplanetary medium at about 1000 km above sea level. Other terms are used to characterize the atmosphere, including the *homosphere*, from the Earth's surface up to the top of the mesosphere at 85 km, in which the permanent gases are found in approximately the same relative proportions; the *heterosphere* above the homosphere, where atomic oxygen (O) and N atoms become increasingly important; and the *ionosphere*, an electrified region extending

from within the mesosphere up through the thermosphere, which contains significant numbers of ions and free electrons.

2.2.1.1 Troposphere

The atmospheric layer closest to the Earth's surface is the *troposphere* (Figure 2.1). Weather conditions (i.e., temperature, precipitation, wind, etc.) that influence our daily lives are confined to this layer, which varies in height from about 18 km above sea level at the equator to about 8 km above sea level at higher latitudes closer to the Earth's poles. At a particular latitude, the troposphere is usually thicker in the summer and thinner in the winter seasons. The troposphere contains most of the atmospheric mass and includes 99% of atmospheric water vapor, which is highest and more concentrated at the equator and decreases toward the polar regions.

Pressure and temperature variations in the troposphere and other major atmospheric regions are shown in Figure 2.1. Atmospheric pressure decreases exponentially with increasing altitude above sea level. In addition, air density also decreases exponentially with altitude, such that about one half of the total number of molecules in the atmosphere is found below 5.5 km above sea level. Average temperatures decrease with altitude in the troposphere (15 to -60°C) with an average lapse rate of about $10^{\circ}\text{C}/\text{km}$. Decreasing temperature with height above sea level is governed by diabatic processes (radiative absorption and emission). The troposphere is mainly heated by *conductive processes* at the planetary surface that are coupled with *adiabatic compression*, causing heating of sinking air parcels. Conversely, adiabatic decompression causes cooling of rising air parcels. Thus, air temperature in the troposphere varies considerably with time of day and season, latitude, and altitude. A shallow transitional zone known as the *tropopause* separates the troposphere from the stratosphere and is characterized by temperature that is constant (an isothermal zone) with increasing altitude. The low temperatures effectively freeze-dry the air in this cold zone, thereby preventing water vapor from being transported from the troposphere into the stratosphere.

2.2.1.2 Stratosphere

Above the troposphere and tropopause lies the *stratosphere*, located approximately 20 to 45 km above sea level (Figure 2.1). Whereas the temperature decreases with increasing altitude in the troposphere and is fairly constant in the tropopause, the stratospheric temperature increases (-60 to 0°C) with altitude due to the absorption of solar UV radiation by ozone (O_3). About 90% of the atmosphere's O_3 content is in the stratosphere. However, the water content of this layer is very low. Although the maximum O_3 concentration (~ 12 ppmv O_3) is generally just above the tropopause at approximately 25 km, the highest temperatures are found in the upper stratosphere. This is due to greater absorption of incoming radiation and lower atmospheric density within the upper stratosphere.

Ozone production is a natural process in the stratosphere and results from the combination of molecular O_2 and atomic O derived from photo-dissociation of O_2 . Destruction of O_3 occurs through collisions with other atoms and molecules. Gases that are especially destructive to O_3 include NO and NO_2 , known collectively as nitrogen oxides (NO_x), and chlorofluorocarbons (CFCs); NO_x is the result of both natural and human (anthropogenic) activities, whereas CFCs are entirely human-made (synthetically produced). A simplified illustration of how CFCs react in the stratosphere is shown in Figure 2.2. In the middle and upper stratosphere, CFCs are photo-decomposed by solar UV radiation that results in the release of chlorine (Cl) atoms that attack and destroy ozone. While ClO molecules are produced in this process, subsequent chemical reactions regenerate the Cl atoms allowing them to go on and destroy more O_3 in what is termed a *chain catalytic ozone destruction cycle*. Loss of O_3 reduces the stratosphere's absorption capacity for UV solar radiation, which, in turn, could potentially cause increased damage to plant life, a greater incidence of skin cancer in

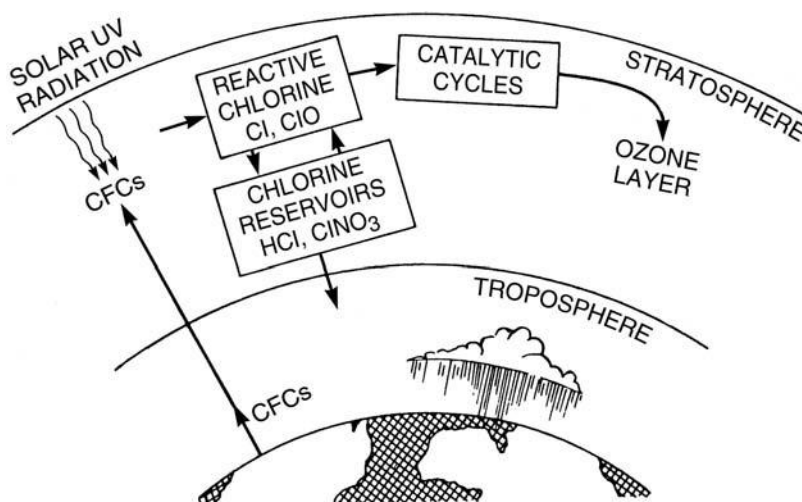


Figure 2.2 Role of CFCs and the degradation products derived from reactions with solar radiation in the reduction of ozone in the stratosphere. (Redrawn from Shen, T. L. et al., in *Composition, Chemistry, and Climate of the Atmosphere*, Van Nostrand Reinhold, New York, 1995. With permission.)

humans, and changes in troposphere chemistry (see Chapter 11 for more information on global climate change and acid deposition impacts involving NO_x and O_3). Another transitional zone, the *stratopause*, exists between the stratosphere and the next highest layer, called the mesosphere.

2.2.1.3 Mesosphere

Above the stratosphere and stratopause is the *mesosphere*, which extends from approximately 50 to 80 km above sea level (Figure 2.1). Within this layer, concentrations of both O_3 and H_2O vapors are minuscule, there is very little air, and atmospheric pressure is low. Temperature again decreases with altitude (0 to -95°C) because of a lack of molecules that significantly absorb solar radiation; about 99.9% of the atmospheric mass is below the mesosphere. Although the percentage of N_2 and O_2 in this layer is similar to that of air at sea level, the low density of this air would not provide sufficient O_2 for humans and suffocation would occur in minutes.

2.2.1.4 Thermosphere

The *thermosphere* is the “hot layer” above the mesosphere, both of which are separated by the transitional *mesopause* zone (Figure 2.1). This layer extends from about 90 to 550 km above sea level. Temperature in this layer (-95 to $>1200^\circ\text{C}$) cannot be determined directly due to the low density of the air. In fact, an air molecule in the lower thermosphere may travel a distance of 1 km before colliding with another molecule; in the upper thermosphere molecules may travel 10 km before a collision occurs.

2.2.1.5 Exosphere

The outermost layer beyond the atmosphere is the *exosphere*, which extends to approximately 960 to 1000 km above sea level. This layer acts as a transitional zone between the primary layers of the Earth’s atmosphere and *interplanetary space* and is comprised primarily of hydrogen (H) and helium (He) at extremely low concentrations. This is the region where atoms and molecules are released into outer space.

2.2.2 Atmospheric Cycles

Several elements and compounds have atmospheric components that are part of their overall interchange cycles among soil, hydrosphere, and biosphere ecosystems. Some of the more important elements include carbon (C), N, and S; cycles of N and S are discussed in Chapters 5 and 7, respectively. Figure 2.3 illustrates some of the important reactions involving C as well as O. Chapters 3 and 11 provide additional information on C and CO₂ cycles, respectively, and their role in C sequestration and the greenhouse effect. In this section we describe the basics of important atmospheric cycles, and provide general information to help understand their interaction with soil, water, and the biosphere.

Oxygen plays an important role in *elemental cycles* (i.e., C, N, P, S, and some trace elements), particularly for those elements that have atmospheric components (C, N, and S). Oxygen is a key element in atmospheric, geochemical, and life processes. Figure 2.3 indicates some of the various chemical reactions and fluxes involved in the O₂ cycle. Atmospheric O₂ (1.18 teragrams; Tg = 10²¹ g) represents the largest O₂ pool, currently in steady state due to a balance between consumption and production processes. It has been suggested that all the O₂ in the atmosphere has been cycled through *photosynthetic organisms* such as plants and specific microorganisms. A large pool of oxygen exists in the *lithosphere* in reduced forms that are slowly released by weathering reactions. Oxygen is also consumed during the burning of fossil fuels, aerobic degradation of organic matter, as well as the oxidative weathering of soil, rocks, and minerals.

Both the O₂ and CO₂ cycles are regulated to a large extent by living organisms. The *turnover rate* or lifetime of O₂ and CO₂ in the atmosphere is related primarily to photosynthesis and respiration processes, which are regulated by plants, humans, animals, and microorganisms. The time required to cycle O₂ and CO₂ through the atmosphere is different due to variation in their persistence and

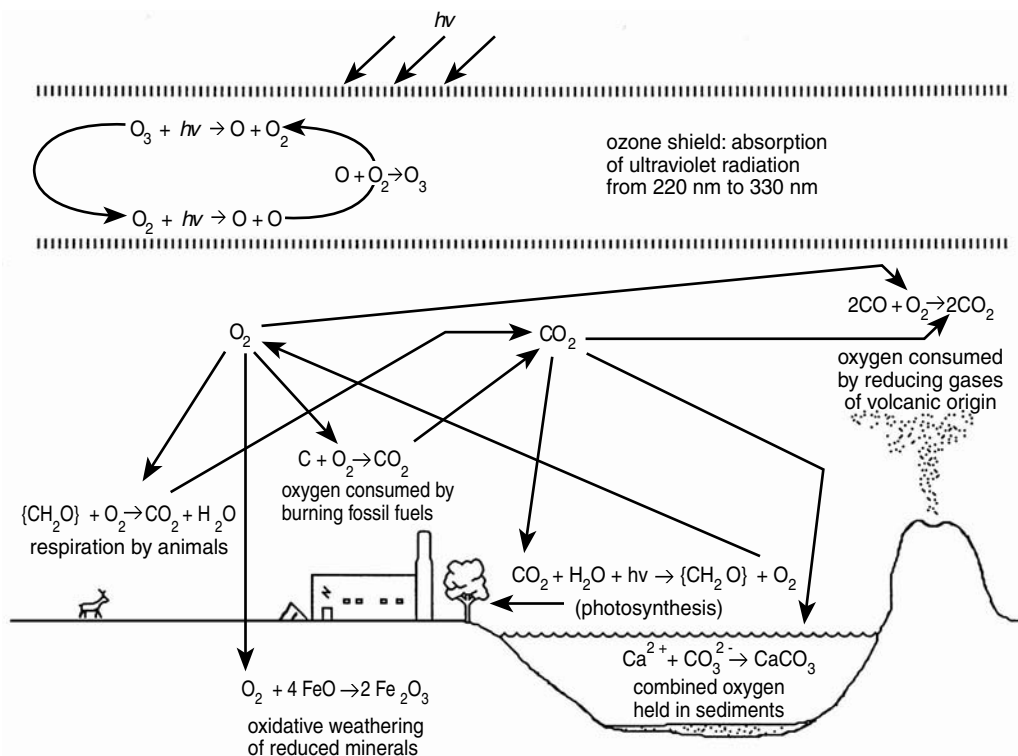
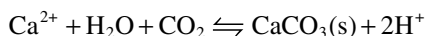


Figure 2.3 Examples of various oxygen and carbon dioxide reactions that occur in the environment. (Modified from Manahan, 1999.)

size of their respective pools. The *mean residence time* (MRT) is a measure of the time it takes a substance to cycle through a particular pool. For example, the MRT of atmospheric O₂ as it cycles through the biosphere is approximately 3000 years, whereas CO₂ MRT is only about 5 years.

Example Problem 2.1

Explain how minerals in waters and soils influence the amount of CO₂ in the atmosphere. Carbonate minerals, e.g., calcite (CaCO₃), contain inorganic carbon that when formed remove CO₂ from water bodies and soil solutions depending on the chemistry of the environment. Therefore, carbonates are believed to be an important sink of C. The formation of carbonate (CO₃²⁻) from CO₂ and the subsequent accumulation of carbonate minerals such as calcite are based on the following simple reaction:



Factors that enhance the formation of CaCO₃(s) are high Ca²⁺ concentrations, alkaline pH (e.g., >7), and low rainfall.

Biogeochemical cycles of nutrients and trace elements can be extremely complex and are often studied by examining individual ecosystems (i.e., atmosphere, hydrosphere, lithosphere, and biosphere). Of primary interest are the specific transfer rates, MRTs, and fates of nutrients, trace elements, and sometimes organic pollutants in one or more of the various ecosystems. Because atmospheric processes influence the cycling of these materials, it is important to understand the relationships among the various constituent pools, their reactions, and fluxes, which are examined in subsequent chapters for N, S, trace elements, and organic chemicals. The influence of human activity on biogeochemical cycles has stimulated several studies that seek to determine what the future may hold for humankind and environmental quality as a consequence of our past and current activities.

2.2.3 Characterizing the Atmosphere

Weather characterizes the state of the atmosphere at a given location and time, whereas *climate* is the summation of averaged weather conditions that distinguish a place or region. Some of the most important parameters that are used to describe weather and climate are air temperature and pressure, type and amount of precipitation and cloudiness, and wind speed and direction. The atmosphere comprises mixtures of discrete gases that change in concentration over time and location. The following sections highlight some of the pertinent features of the atmosphere that are important to understanding conditions that exist in different parts of the United States and why these conditions occur.

2.2.3.1 Air Temperature and Precipitation Patterns

Climate patterns can be quite varied on both regional and global scales. Average climatic parameters have also changed with time due to both natural (e.g., volcanic eruptions) and anthropogenic (e.g., fossil fuel emissions) inputs. For example, there is sufficient evidence today to conclude that the *global average temperature* has been increasing over the past 150 years (see Chapter 11). While there is a certain amount of annual variation in the global temperature, Figure 2.4 indicates there is a definite increasing trend for warmer temperatures in recent years. Annual precipitation patterns are also variable, with reports of occurrences of *1-in-100-year rainfall events* heard often. The global distribution of precipitation is generally related to atmospheric circulation patterns and the location of mountain ranges and high plateaus. We know that areas in the equatorial

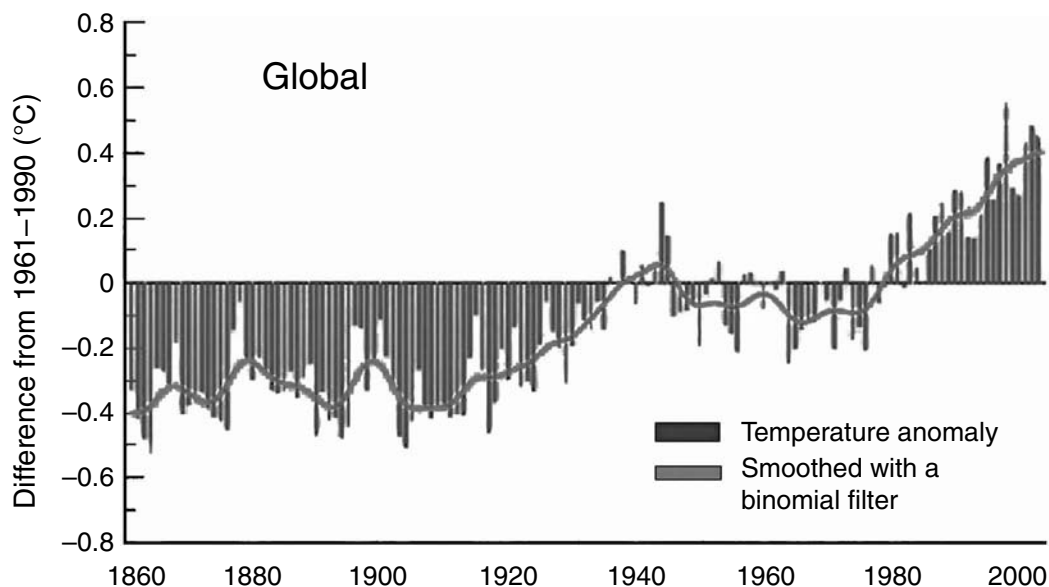


Figure 2.4 Relative annual changes in the global average temperature from 1861 to 2003. Note the large variability between adjacent years (e.g., as much as 0.25°C) and the distinctive increasing trend from 1905–1935 and 1975–present. There has been an approximate 1.0°C increase in the global average temperature since the 1860s.

region are usually the wettest and that the polar regions, leeward sides of mountains, and some areas influenced by subtropical high pressure systems are typically the driest.

Minimum, maximum, and ranges in temperatures and rainfall patterns across the United States are related to many climatic and geographic variables. For example, the topography along a transect from the Pacific Ocean into western Nevada can cause enormous variability in the annual precipitation received within different regions of the transect. Figure 2.5 illustrates how topography results in several “*rain shadow*” effects along the transect. These are regions on the leeward side of mountains that receive conspicuously less precipitation than is obtained on the windward side of mountain ranges. There is a distinct difference in the amount of precipitation on west and east sides of mountain ranges, with amounts two, three, four, or more times greater on windward sides, e.g., compare Mariposa (70 cm) and Yosemite (90 cm) to Bishop (20 cm).

Within the United States, there are tremendous differences in *annual temperature and precipitation* going from the West Coast to East Coast. Western states receive winter precipitation from Pacific Ocean–fed storms that often replenish the loss of water that occurs during hot, dry summers. Intense winter storms traveling eastward can cause major problems in the central United States due to heavy snowfalls; intense summer storms also result in serious flooding events. Because of moisture brought in from the Gulf of Mexico, most of the precipitation in the United States occurs in the eastern states where there is higher average annual precipitation. As noted in Figure 2.6, the western United States (e.g., San Francisco) generally receives greater amounts of precipitation in winter months, the central United States (e.g., Kansas City) obtains mostly summer precipitation, and the eastern United States (e.g., Washington, D.C.) receives abundant precipitation year round. However, it should be noted that there are numerous years that are exceptions to the overall average. Temperature extremes in the United States are evidenced by hot, dry desert conditions in some parts of the West to cold, snowy mountainous regions of Alaska and the Rocky Mountains. Record high and low temperatures for the United States are 57°C (134°F) in Death Valley, CA and -62°C (-80°F) and -57°C (-70°F) in Prospect Creek, AK and Rogers Pass, MT, respectively. The world’s highest and lowest temperatures on record are 58°C (136°F) in Azizia, Libya and -89°C (-129°F) at the Vostok Research Station in Antarctica.

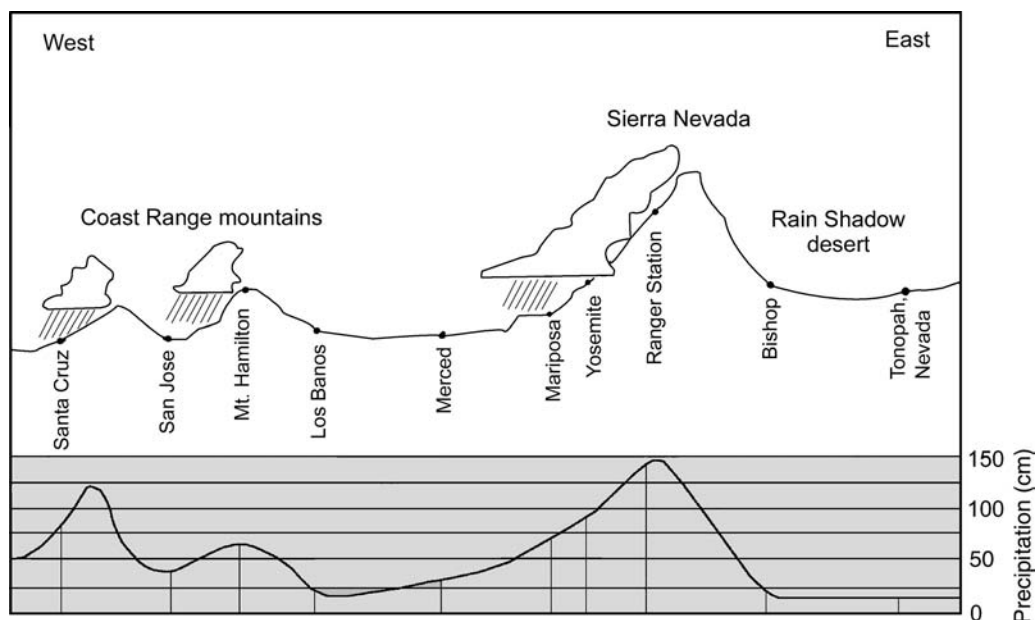


Figure 2.5 Precipitation patterns along a transect from California east into Nevada showing distinct topographical differences and rain shadow effects. (Redrawn from Ahrens, C. D., *Meteorology Today: An Introduction to Weather, Climate, and the Environment*, 5th ed., West Publishing, St. Paul, MN, 1994.)

Typically, temperature and precipitation characteristics for a given location are expressed on a *30-year average*. Currently, the standard 30-year time span is from 1971 to 2000. Temperatures can be characterized by other methods as well. For example, *average daily temperature* is the mean of high and low temperatures for that day, whereas the average temperature for a given length of time is the mean of daily temperatures over that time period. Average high and low temperatures are also frequently mentioned. Average annual precipitation characterizes precipitation for a location, but distribution of that moisture over the year is also important (see Figure 2.6). Finally, rainfall intensity plays a major role in partitioning of water into surface runoff or water that infiltrates into the soil. For example, a 10-cm rainfall event received uniformly over 8 h has an average intensity of 1.25 cm/h and will usually not generate much runoff. The same amount of rainfall received in 1 h, producing an intensity of 10 cm/h, would likely cause considerable runoff, particularly in areas that contain fine-textured (e.g., clay or clay loam) soils. Some areas are more prone than others to short-duration, high-intensity storm events.

Example Problem 2.2

Determine the approximate amount and percentage of precipitation that San Francisco receives during the summer months of June, July, and August. By using Figure 2.6, the approximate amount of precipitation during the summer months is less than 1 cm. With a total annual precipitation of 48 cm, San Francisco receives a total of

$$\frac{1 \text{ cm}}{48 \text{ cm}} \times 100 = \sim 2\%$$

of its precipitation in the summer.

Climatic regions are defined based on temperature and precipitation patterns. Within the United States there are four major climate types with several subdivisions. The West Coast is characterized

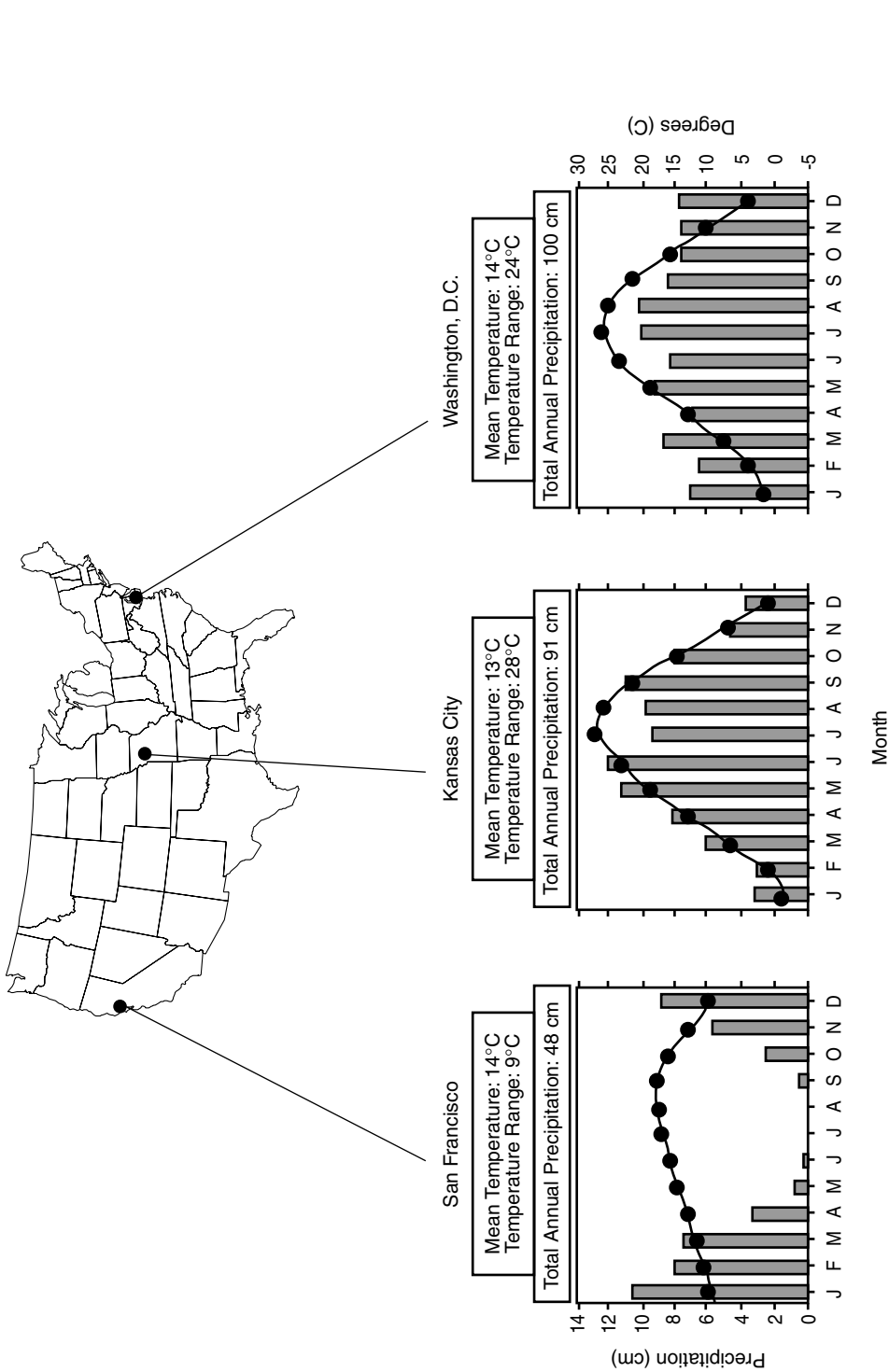


Figure 2.6 Differences in monthly temperature (solid circles) and precipitation (bars) in West Coast, Central, and East Coast cities. Note the distinct difference in precipitation, with San Francisco receiving a majority of its precipitation in winter and Washington, D.C. receiving fairly constant precipitation year round.

as a moist climate with either long, cool or hot, dry summers. Moving east are the highlands or mountains that have cold temperatures year round, and include the Sierra Nevada and Rocky Mountains. Between the highlands are dry climate regions that are arid and semiarid and vary from hot to cool temperatures, which is primarily a function of altitude. The Great Plains region is classified as a dry climate with cool mean annual temperatures. The northeastern quarter of the United States has a moist climate with severe winters and humid summers, whereas the southeastern United States, the largest climatic region, has a moist climate with mild winters and humid subtropical summer conditions.

2.2.3.2 Wind Speed and Direction

Wind results from atmospheric (or air) pressure differences, with wind speed and direction dependent on the extent of the horizontal variation in atmospheric pressure (*pressure-gradient force*), the deflection effect due to the Earth's rotation (Coriolis effect), and friction with the Earth's surface. *Wind speeds* are to a large degree a function of acceleration of air from regions of high pressure to regions of low pressure. In addition to its influence on wind, atmospheric pressure also is associated closely with, and has a considerable influence on, weather variables such as temperature and humidity as well as the dispersal of atmospheric pollutants. The *Coriolis force* alters the direction of wind with winds rotating around low-pressure centers (cyclones) counterclockwise and clockwise, respectively, in the Northern Hemisphere and Southern Hemisphere. Friction is most important within a few kilometers of the Earth's surface where wind speeds are reduced. Both wind speed and direction can be measured using an *aerovane* that contains both an *anemometer* (speed) and *wind vane* (direction).

Average wind speed and direction for a given location can be graphically represented with a *wind rose* (Figure 2.7). The wind rose depicted in Figure 2.7 is for Dodge City, KS (noteworthy as the windiest place in the continental United States). The rose tells us that the wind blows most often from the south, followed by south by southeast, north, and then south by southwest; wind

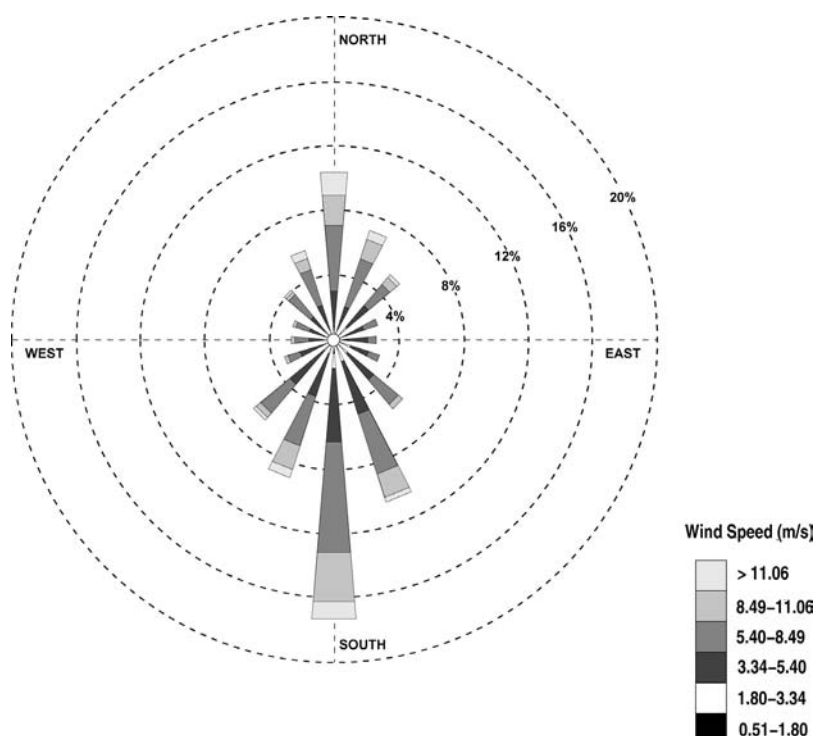


Figure 2.7 A wind rose for Dodge City, KS that depicts the frequency of wind direction and speed.

blows infrequently from due east or west. Within each bar the relative amount of time the wind blows in that direction at a particular speed is depicted. When the wind blows out of the north or south, for example, the wind speed frequently exceeds 11 m/s (~25 mph). A wind rose can assist with tracking a *contaminant plume* for a pollutant discharge from a point source (e.g., a smokestack) or other relatively concentrated sources of an airborne contaminant.

At sea level, average atmospheric pressure is about 1 kg/cm² (or 14.7 lb/in.²). However, measurements are usually given as “inches of mercury” based on a mercury *barometer*, or are reported as millibars of pressure by professional agencies, with a standard sea level pressure of 29.92 in. or 1013.25 mb, respectively. Changes in atmospheric pressure are often related to the type of weather conditions that can be expected for a particular region. For example, if air pressure decreases, we could anticipate increasing cloudiness and the possibility of precipitation, whereas increasing air pressure suggests favorable clearing conditions. Air pressure differences are fundamentally related to the unequal heating of the Earth’s land and sea surfaces.

Wind chill temperatures are related to actual air temperature and the fact that windy conditions can enhance the loss of sensible heat from humans and animals. The stronger the winds, the greater the wind chill effect, as noted by how cold the temperatures feel. For example, at a wind speed of 65 km/h (40 mph) and a temperature of –15°C (5°F), the wind chill temperature would be –30°C (–22°F). Measurements of wind chill temperatures have changed recently after tests conducted on humans determine temperature differences between external body temperatures to those inside the mouth and rectum for gradient and body temperatures, respectively. The old method of calculating wind chill temperatures often predicted temperatures lower than what people really felt. Cold temperatures are noted for reducing the reaction time required for pollutant degradation. This is true for atmosphere, soil, and aquatic environments where pollution has occurred.

2.2.3.3 Chemical Composition

Chemical constituents making up the majority of lower atmospheric gases are N₂ (78.08%), O₂ (20.95%), and argon (Ar) (0.93%), which together comprise more than 99.9% (by volume) of the composition of air. Water vapor in the atmosphere is highly variable, changing with altitude, latitude, and temperature. Different phases of H₂O (e.g., solid, liquid, and gas) are important to various weather conditions as well as to heat storage and release. Carbon dioxide, methane (CH₄), NO_x, sulfur dioxide (SO₂), O₃, and CFCs, although only minor in abundance, are particularly important to the chemistry of the Earth’s atmosphere and to environmental issues such as *global climate change* and *acidic deposition* (see Chapter 11). A detailed summary of the average global composition of the atmosphere is given in Table 2.1.

Both N₂ and O₂ are continually being lost from and released into the atmosphere, with their rate of removal balanced by an approximately equal level of production. Molecular N₂ gas is relatively inert, but through *biological N fixation* processes, organic N forms are produced that are sources of nutrients and structural components to living organisms (see Chapter 5). Conversely, decomposition of plant and animal remains, as well as biochemical reduction of soluble N species, releases N₂ back into the atmosphere. Oxygen is used during decomposition, respiration (O₂ is inhaled, CO₂ is exhaled), and combustion processes. During plant growth, sunlight provides energy for production of sugars and O₂ from the combination of CO₂ and H₂O, a process known as photosynthesis. Approximately 1% of the Sun’s energy that reaches the Earth’s surface is used during photosynthesis; most of the incoming solar energy is absorbed by the Earth’s surface, with a significant fraction used in the evaporation of water, resulting in latent heat release during subsequent cloud formation.

The chemical composition of the lower atmosphere is relatively homogeneous, except in areas close to the Earth’s surface that are affected by air pollution. Mixing takes place in the troposphere due to winds and rising of warm air that develop near the Earth’s surface, which promotes homogenization (dilution and dispersion of different chemical constituents) of the atmosphere. *Inversions*

Table 2.1 Global Average for Chemical Constituents in the Atmosphere

Chemical Constituent	Common Name	Percent by Volume	Approximate Mass (kg)
	Dry air	100	5.12×10^{18}
Permanent Gases			
N ₂	Nitrogen	78.08	3.9×10^{18}
O ₂	Oxygen	20.95	1.2×10^{18}
Ar	Argon	0.93	6.6×10^{16}
Ne	Neon	1.8×10^{-3}	6.5×10^{13}
He	Helium	5.2×10^{-4}	3.7×10^{12}
H ₂	Hydrogen	5×10^{-5}	1.8×10^{11}
Variable Gases (most of these values are estimates)			
H ₂ O	Water vapor	0.1–4	1.70×10^{16}
CO ₂	Carbon dioxide	3.5×10^{-2}	2.45×10^{15}
CH ₄	Methane	1.5×10^{-4}	4.3×10^{12}
N ₂ O	Nitrous oxide	3×10^{-5}	2×10^{12}
CO	Carbon monoxide	1×10^{-5}	6×10^{11}
NH ₃	Ammonia	1×10^{-6}	3×10^{10}
NO _x	Nitrogen oxides	1×10^{-7}	8×10^9
SO ₂	Sulfur dioxide	2×10^{-8}	2×10^9
H ₂ S	Hydrogen sulfide	2×10^{-8}	1×10^9
O ₃	Ozone	0.01–25 ppm	3×10^{12}
CFCs	Chlorofluorocarbons	0.002 ppm	Variable

Note: Total atmospheric mass equal to 5.14×10^{18} kg.

Sources: Walker, 1977; Ahrens, 1994; Salstein, 1995.

(i.e., temperature increases with altitude) prevent mixing and cause the air to retain pollutants, a condition that is sometimes noticed during the night and early morning when wood smoke from chimneys does not dissipate readily. Topographic lows and urban areas are also known to prevent atmospheric mixing that homogenizes the local air mass. Within the stratosphere, only minor changes in chemical composition occur over short time periods because very little vertical mixing takes place.

2.2.4 Atmospheric Pollution

The high relative concentration of N₂ and O₂ in the atmosphere ensures that their abundances are not subject to significant perturbation. Percentages of the other *atmospheric constituents*, however, change with time as a result of natural and anthropogenic emissions. Atmospheric pollutants tend to be higher over source areas such as cities and fossil fuel-burning power plants. Additionally, there are natural sources that emit gases; swamps and anaerobic environments release CH₄ and hydrogen sulfide (H₂S), and wildfires can cause the emission of CO₂, carbon monoxide (CO), CH₄, and carbonyl sulfide (COS). Agricultural practices are partially responsible for CO and N₂O releases from cultivation and fertilization of soils. Even domestic ruminant animals contribute approximately 60 to 100 Mt (Mt = megagrams, Mg) of CH₄ per year, accounting for about 15% of the CH₄ emitted globally.

Humans have had a profound effect on atmospheric composition. Some trace gases that have increased due to human activities include CO₂, CH₄, N₂O, CO, and CFCs. These gases can either directly or indirectly increase the amount of absorption of infrared radiation, thus intensifying the *greenhouse effect* (see Chapter 11 for further discussion on global climate change). Although there is sufficient controversy related to the extent of climate change and global warming, there is ample evidence that indicates pollutant gases and particulates are entering our atmosphere from burning fossil fuels, removal of natural vegetation, release of CFCs, and other human activities.

Atmospheric CO₂ concentrations have increased by about 30% over levels determined from preindustrial times, prior to 1800. Between 1958 and 2004, the level of atmospheric CO₂ rose from 316 to 373 ppmv, a rate of increase of more than 1 ppmv/year. Under the scenario of “business as usual,” CO₂ concentrations will double that of the preindustrial level by the middle of this century. Business as usual refers to our continued reliance on burning fossil fuels that produce CO₂ and our clear-cutting of temperate and tropical forests, which decreases CO₂ consumption by photosynthesis. Increasing levels of atmospheric CO₂ and other greenhouse gases are expected to result in a rise in *global mean temperatures* by 1.5 to 5°C sometime between 2025 and 2050 (see Chapter 11).

In addition to atmospheric gases, particulate matter comprising various organic or inorganic materials consisting of liquids or solids is also present in the atmosphere. Biological materials such as viruses, bacteria, spores, and pollen grains are classified as particulate matter if suspended in the atmosphere. *Particulate matter* is generally smaller than 0.5 mm and can be derived from several natural and anthropogenic sources. Most particles are, however, smaller than 0.001 mm. Particles less than 1 mm are capable of being retained in the atmosphere and transported long distances. Particles in the range of 0.00001 to 10 mm are common in and around pollution source areas such as cities, highways, industrial operations, and power plants. Winds can greatly reduce the concentration of these materials within short distances of their sources.

Airborne particles can originate from explosions, breakdown of materials by grinding action, volcanic activity, wind erosion, and from the condensation of gaseous precursor pollutants. Surface mining relies on explosives to loosen the underlying rock so that it can be removed or processed. Large amounts of particulate matter can result from wind erosion in arid and semiarid areas. As an example, windblown soil particles from arid regions have been estimated to contribute 10³ Tg of particulate matter to the atmosphere each year. Of this, 20% is less than 1 mm and can be transported over long distances. *Particulate matter less than 2.5 μm (PM_{2.5}) or 10 μm (PM₁₀)* are commonly measured in air. Particles in these size categories can be drawn deep into lung tissue and can represent a health hazard.

Trace elements are added to the atmosphere by several processes. Fossil fuel and coal burning, smelting of iron (Fe) and nonferrous metals, volcanic ash, and wind erosion are responsible for increasing atmospheric concentrations of such elements as bromine (Br), cadmium (Cd), gold (Au), lead (Pb), selenium (Se), tin (Sn), and tellurium (Te) by as much as four orders of magnitude above normal levels. Concentrations of trace elements can be bioaccumulated by some plants and microorganisms, possibly increasing the potential harmful effects of trace elements. Trace element types, characteristics, and effects are discussed further in Chapter 9.

The concept of an airshed is often used to characterize the potential for atmospheric deposition of contaminants in a watershed or water body. Generally these areas are sensitive to one or more contaminants. The contaminants of greatest concern would be nutrients, pesticides, select organic chemicals, and acidic materials. An *airshed* is defined as an area of land that represents or contains potential sources of airborne contaminants that may affect a given watershed or water body. A given watershed or water body may have a different airshed for each contaminant, reflecting the diverse sources for airborne contaminants and the complicated mechanisms by which contaminants are transported through the troposphere. Airsheds can be used as a management tool to decrease atmospheric deposition. Once the airshed has been delineated, efforts can be made to address contaminant sources. Excellent examples would be atmospheric deposition of N into the Chesapeake

Bay or N deposition in Rocky Mountain National Park due to air pollution originating from the Front Range of Colorado. Nutrient enrichment from N is currently resulting in a negative effect on the aquatic ecosystems in the bay as well as forests and streams within the park.

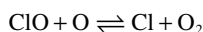
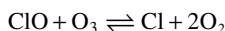
Environmental Quality Issues/Events

Chlorinated Gases and the Ozone Hole

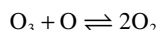
Concerns associated with *stratospheric O₃ depletion* are most evident over Antarctica (South Pole); however, a smaller O₃ thinning is also apparent in the Arctic (North Pole), and to a lesser extent in mid-latitudes. British scientists collecting data in the Antarctic beginning in 1950 discovered a seasonal O₃ fluctuation that probably started in the 1960s. Their research discovery indicated there was a progressive thinning of the O₃ layer, especially during spring months, with lowest levels typically recorded in mid-October (remember that spring in the Southern Hemisphere is fall in the Northern Hemisphere). Research conducted using high-altitude airplanes, satellites, and instrumented balloons released over the Antarctic discovered that there was nearly a 40% reduction of O₃ in the spring of 1984 that increased to about a 70% depletion by 1993. During an extreme period in 1993, an area with at least 50% O₃ depletion was approximately three times as large as the continental United States. On a global scale, 5% or more of the Earth's O₃ has been depleted since the early 1980s.

Chlorinated gases are believed to be one of the primary substances that cause destruction of the O₃ layer. Researchers discovered in 1972 that rocket engine emissions in the stratosphere were a potential cause of local O₃ destruction, with the primary chlorinated gas (hydrogen chloride, HCl) released in large quantities. Two years later it was realized that other chlorinated gases such as CFCs could significantly exacerbate the problem. *Chlorofluorocarbons* (e.g., Freon™) were first developed in the 1930s by du Pont Industries as supercoolants that, at the time, were perceived to be inexpensive, noncorrosive, nonflammable, and nonreactive (e.g., chemically stable). Freon has been used as a coolant for refrigerators and air conditioners, as well as an aerosol spray propellant for spray paints, hair spray, whipped topping, cosmetics, insecticides, and other materials.

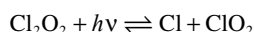
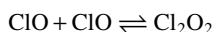
Within the Antarctic stratosphere, ice crystals (polar stratospheric clouds) form in the winter months that promote the formation of chlorine gas (Cl₂) from HCl, hypochlorous acid (HOCl), and chlorine nitrate (ClONO₂) that are absorbed on their surfaces. The return of sunlight, after 6 months of long polar nights, causes the photo-decomposition of Cl₂, creating a bloom of Cl atoms that attack O₃. Chlorine is extremely effective at destroying O₃ molecules according to the following catalytic reaction series:



with the net result:



It is essential to note that all of the important *O₃-destroying catalytic cycles* involving chlorine include the *chlorine monoxide* (ClO) species. An additional reaction involving ClO that results in regeneration of chlorine atoms is



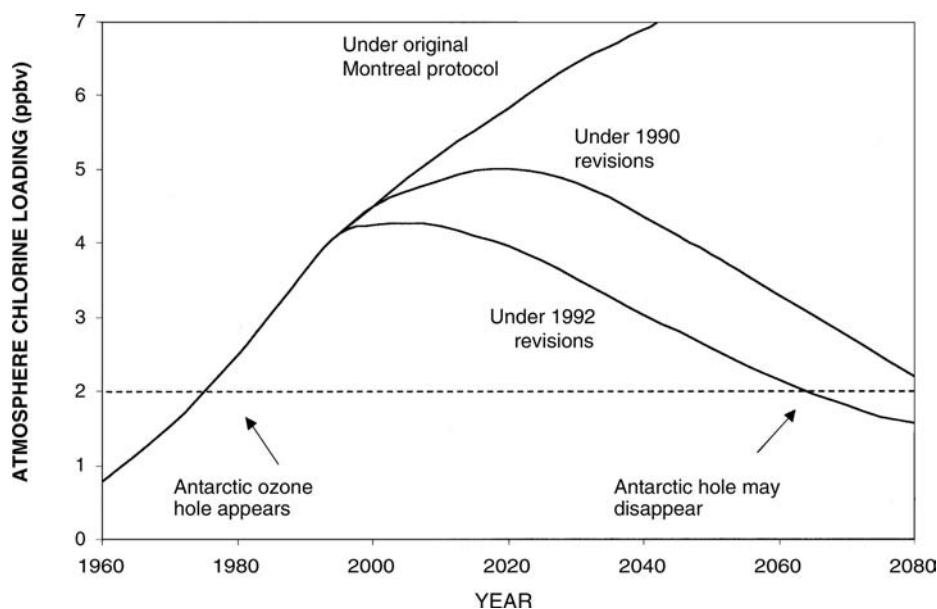
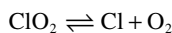


Figure 2.8 Atmospheric Cl concentrations (1960–1990) and the expected change due to the Montreal protocol for reducing Cl loadings. Note that 2 ppbv Cl is the theorized stratospheric limit that is required for the appearance of the Antarctic O₃ hole.



One Cl atom photo-dissociated from a CFC molecule can catalyze thousands of O₃-destroying cycles, resulting in the degradation of about 100,000 O₃ molecules. With an estimated 20 Tg of CFCs produced since their introduction, and with about 90% released into the atmosphere, it is no wonder the use of CFCs had to be reduced.

In recognizing the potential problems associated with CFCs, industry started to produce CFC-free propellants for spray cans and assisted in supporting an intense research program aimed at finding alternatives to the use of CFCs as refrigerants. An international conference in 1987 resulted in the “Montreal Protocol on Substances That Deplete the Ozone Layer” that was accepted by many nations as a way to curtail the problem. As shown in Figure 2.8, the original protocol, which mandated a reduction in the consumption of five CFCs to 50% of 1986 concentrations and three Br-containing halocarbons to 1986 concentrations by the year 2000, was deemed insufficient for reducing the O₃-damaging substances. Revisions to the Montreal protocol were negotiated in London (1990), Copenhagen (1992), Vienna (1995), Montreal (1997), and Beijing (1999). From Figure 2.8 it is apparent that declines in global O₃ levels will continue for some time to come, and that the “ozone hole” over Antarctica will continue to develop every year for most of the 21st century.

2.3 HYDROSPHERE

The *hydrosphere* includes water bodies such as rivers, streams, lakes, and oceans as well as soil water, groundwater, glaciers, and polar ice caps (Figure 2.9). Although approximately 70% of the Earth’s surface is covered with water, an enormous amount of water is found belowground. By far the largest source of water is in oceans and seas, followed by ice (polar ice caps and glaciers) and then groundwater. Freshwater and saline lakes and inland seas represent the largest

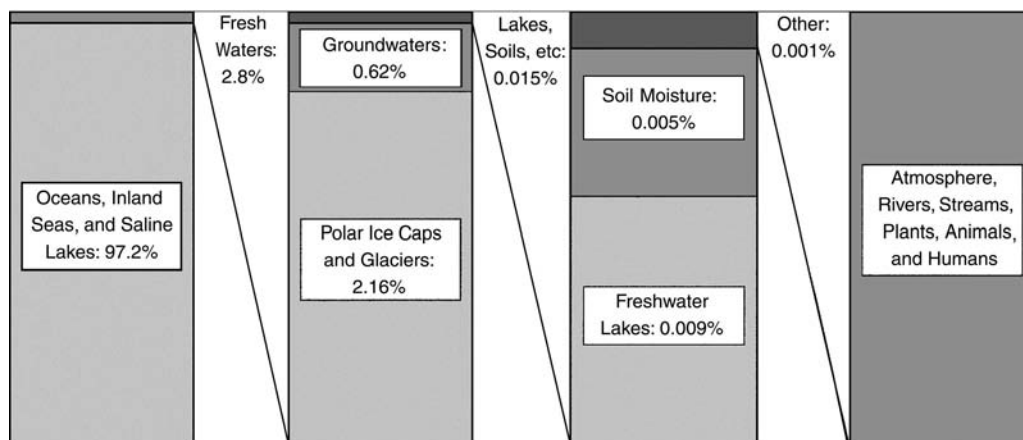


Figure 2.9 Categorization of hydrosphere pools ranging from the dominant sources on the left to those that comprise smaller sources on the right.

pools of liquid water on land, with rivers and streams comprising only a small fraction of the world's water. The amount of water retained in soils is approximately 50 times greater than that in rivers and streams. While the atmosphere contains only a small fraction of the total amount of water held in other pools, the quantity of water that passes through the atmosphere is immense and extremely important.

The study of the chemical, physical, and biological properties and reactions of water bodies is called *hydrology*; *limnology* is the study of freshwater systems; *oceanography* the study of oceans; and *meteorology* the study of climate and weather, which is highly dependent on water in the atmosphere as noted in the previous section. *Geohydrology* is the study of water in geological systems such as aquifers and groundwater environments. Soil scientists also study the chemical, physical, and biological properties of soil ecosystems in which water plays a dominant role.

2.3.1 Properties of Water

Water is essential to all forms of life on Earth. It is also the central component to several soil processes. Ice can physically break rocks into small particles that can then be further weathered by chemical processes. Dissolution of soil minerals and the migration of the dissolved materials is a continual process that is driven by water leaching through soils. In areas of low rainfall, weathering and translocation of dissolved constituents is relatively slow compared with high rainfall areas. Transport of contaminants from soils to groundwaters or surface waters is generally accelerated as the amount of water that percolates through the soil increases.

Water, which is often referred to as the “universal solvent,” is essential for the transport of nutrients, gases, and organic compounds in the soil environment. Some of the unique properties of water are listed in Table 2.2. Many of these properties are the result of the molecular structure of water and its ability to form H bonds. *Hydrogen bonding* allows water molecules to interact with one another and form clusters or liquid crystals. These interactions give water unique characteristics that set it apart from other molecules of similar size and weight. For example, CH₄ (molecular weight of 16) changes from a solid to a liquid at -182°C and from a liquid to a gas at -55°C , whereas phase changes for water (molecular weight of 18) occur at 0°C and 100°C for solids to liquid and liquid to gas transformations, respectively. Without the strong interactions between water molecules, water would be a gas at temperatures higher than -80°C (-112°F) and freeze at -150°C (-238°F), and there would be no liquid forms of water on Earth!

Table 2.2 Water Properties, Significance, and Distinctions

Property	Significance	Distinction
Solvent	Essential for many biochemical, chemical, geological, and atmospheric processes	Ubiquitous substance
Density	Allows ice to float on water	Maximum density at 4°C
Dielectric constant	Reason most ionic substances at least partially dissolve in water	Highest of all pure liquids
Surface tension	Produces unequal attraction forces between two phases	Highest of all liquids
Heat of evaporation	Controls rate of heat and water transfer between water and atmosphere	Highest of all substances
Latent heat of fusion	Stabilizes temperature change at freezing point	Highest of all liquids except NH ₃
Heat capacity	Balances temperature changes	Highest of all liquids except NH ₃
Transparency	Allows transfer of sunlight to great depths in water bodies where it is required by photosynthetic organisms	Colorless substance

Source: Adapted from Manahan, 1999.

Water expands when it freezes; no other common liquid has this characteristic. Therefore, ice has a lower density than liquid water, which is the reason ice forms on the top of lakes and icebergs float in the cold oceans and seas. Imagine the consequences if the density of ice were higher than liquid water. What would happen to freshwater lakes if they froze solid? From a soil science point of view, freezing and thawing play an important role in soil formation, erosion, and structural problems (e.g., cracking and heaving). In addition, the high specific heat of water results in greater amounts of energy required to raise the temperature of water. This causes water to heat up and cool down at a much slower rate than all other liquids, except ammonia (NH₃). Because water is such a good solvent, and has the ability to dissolve most substances, there is a greater chance for contaminants to remain soluble for longer periods of time once they are dissolved in a water body.

2.3.2 Components of the Hydrologic Cycle

Water transfer or movement from one environment to another governs the *hydrologic cycle* (Figure 2.10). Water enters the atmosphere primarily through evapotranspiration processes (e.g., combination of water evaporation from soils and water bodies and the transpiration by plants) and is returned to ocean and land surfaces in the form of rain, fog, hail, and snow. The rate of water transferred from one pool to another, which is called *water flux*, is shown in Figure 2.11. Generally, the quantity of water leaving a water source is compensated for by the amount of water entering the source. The rates shown are estimates for current water fluxes that have changed during the evolution of the Earth.

Water-soluble pollutants entering pools with low MRTs may be rapidly transported to another ecosystem over short periods of time. The pollution potential of a substance is related to its water-soluble characteristics, harmful nature, and the MRT of a particular aquatic system. Thus, if an accident resulted in a contaminant spillage into a river (or other water body with a low MRT), and the contaminant is highly soluble, it could rapidly be transferred to another pool. If the MRT in the receiving pool is large, then the contaminant may remain in this pool for a longer period of time, causing long-term problems.

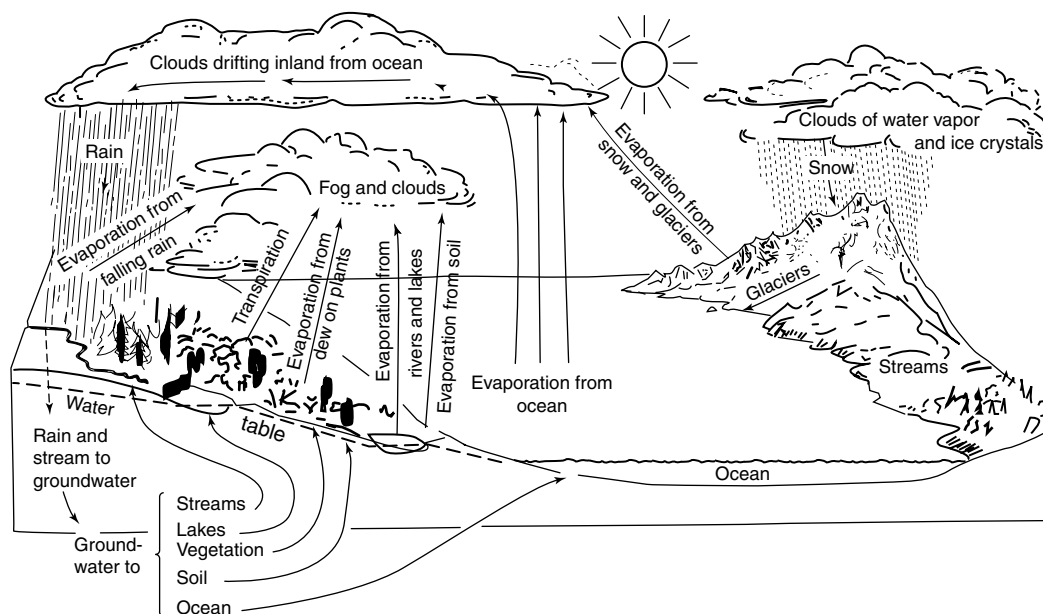


Figure 2.10 Illustration of the various pools and transfer processes that occur in the hydrologic cycle. (Modified from Gilluly, J. et al., *Principles of Geology*, 4th ed., W. H. Freeman, San Francisco, 1975. With permission.)

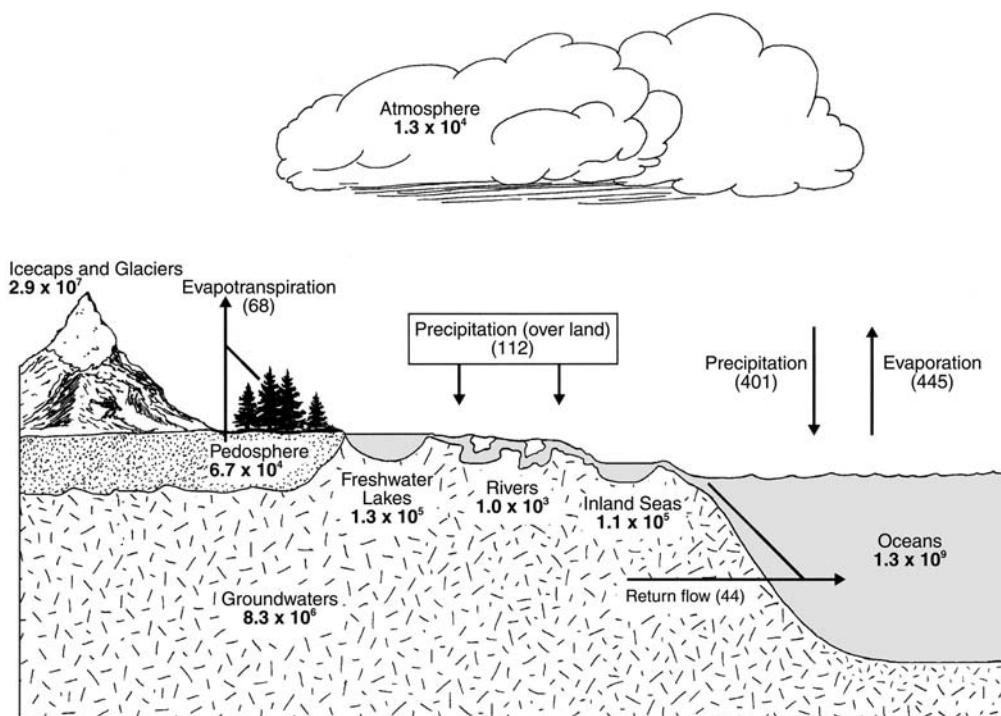


Figure 2.11 Content of water in various hydrosphere pools (bold numbers, km³) and global transfer rates (in parentheses, 10^3 km³/year) for water movement in the hydrologic cycle. (Information obtained from the U.S. Geological Survey Web site, <http://water.usgs.gov/data.html>.)

Example Problem 2.3

The MRT for water in various pools can be calculated if it is assumed that input is equal to output, and if the mass of water in the pool and rates at which water is entering and exiting the pool are known (i.e., $MRT = \text{mass/flux}$). Using the information in Figure 2.11 we can calculate MRT for various pools. For example, MRT for water in the atmosphere would be

$$MRT = \frac{13,000 \text{ km}^3}{513,000 \text{ km}^3/\text{year}} = 0.025 \text{ years or 9.2 days}$$

The fast rate at which water moves from land to oceans in rivers results in a MRT for streams and rivers of

$$MRT = \frac{1,000 \text{ km}^3}{44,000 \text{ km}^3/\text{year}} = 0.023 \text{ years or 8.3 days}$$

As a comparison, the MRT of water in the ocean is

$$MRT = \frac{1,320,000,000 \text{ km}^3}{445,000 \text{ km}^3/\text{year}} \approx 3,000 \text{ years}$$

Finally, MRTs of water in lakes and groundwater systems have been estimated to be tens of years to hundreds or thousands of years, respectively.

2.3.2.1 Inland Surface Water

Inland surface waters include streams, rivers, and lakes. In general, water entering lakes, bays, and estuaries comes from the surrounding area, which is known as its watershed or drainage basin. Sources of water entering streams and rivers can include rainfall, surface runoff during periods of high rainfall, lateral water movement below the soil surface due to topography or stratified layers of different textures, water stored in adjacent wetlands areas, or from groundwater sources. Several natural (e.g., climate, vegetation, physiography, geology) and human (e.g., urbanization, agriculture, deforestation) factors influence the quality and quantity of water in inland surface water bodies.

2.3.2.2 Soil Moisture

Infiltrating water can move below the soil surface into a region known as the *vadose zone* (unsaturated region) or move even deeper into the *groundwater zone* (saturated region) (Figure 2.12). The upper surface of the groundwater zone is called the *water table*, which fluctuates depending on the amount of water received by, or depleted from, the groundwater zone. The *capillary fringe* is the area above the water table where water in small pores is drawn upward by capillary action. Water movement in soils is due to a combination of (1) hydraulic gradients and (2) the ease with which water moves through soil or rock (hydraulic conductivity) (see Chapter 3 for more information on soil water).

2.3.2.3 Groundwater

Groundwater is used for several purposes. *Groundwater resources* are the world's third largest source of water and represent 0.6% of the Earth's water content. Approximately 53% of the U.S.

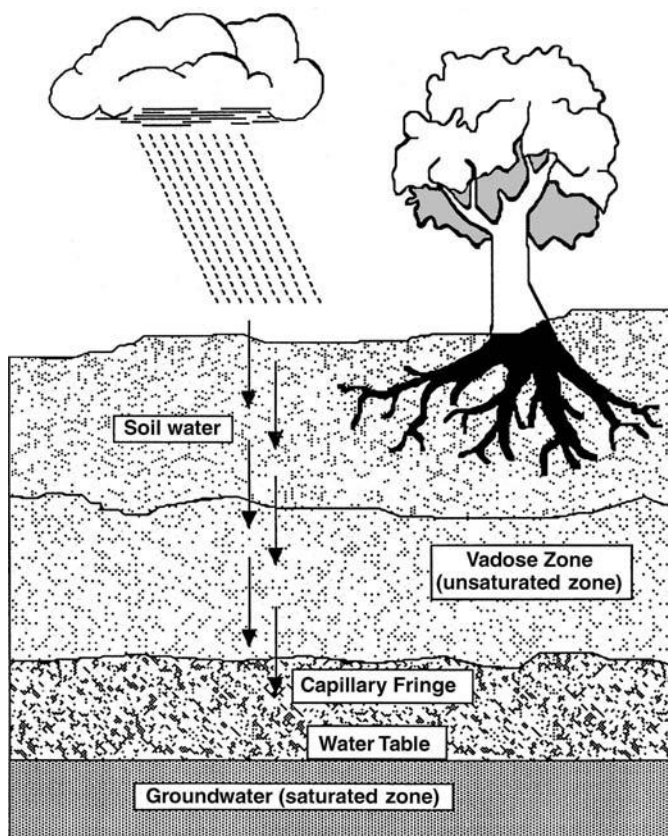


Figure 2.12 Saturated and unsaturated subsurface soil water zones. Unless drainage is restricted, most soils are unsaturated and hold water by adsorption and capillary forces.

population uses groundwater as a drinking water source, but this percentage increases to almost 97% for rural households. In areas of low rainfall, weathering and translocation of dissolved constituents are relatively slow compared to high-rainfall areas. In addition, physical disruption of rocks into small particles can enhance mineral weathering, which results in mineral dissolution and migration of dissolved substances. Transport of contaminants from surface and subsurface environments to groundwaters is generally accelerated as the amount of percolating water increases. Important hydrogeological characteristics of a site that determine groundwater quantity and quality are listed in Table 2.3.

Groundwater movement responds to gradients, which are a function of gravitational forces and the permeability of substrata materials. Substrata are characterized by their *porosity* and *permeability* that together represent the degree of void space and resistance to water movement. Thus, groundwater moves faster in coarse-textured substrata and as the slope of the water table increases. *Aquifers* are groundwater systems that have sufficient porosity and permeability to supply enough water for a specific purpose. In order for an aquifer to be useful, it must be able to store, transmit, and yield sufficient amounts of good-quality water. Aquifers are classified as either confined (located under an impermeable substrata material) or unconfined (unrestricted above and having a water table). There may be enough pressure built up in a confined aquifer to create artesian conditions. Regions of substrata material that have low permeability and do not yield sufficient amounts of water to be practically useful are called *aquicludes* or *aquitards*.

Table 2.3 Important Hydrogeological Characteristics of a Site That Determine Groundwater Quantity and Quality

Geological	
Type of water-bearing unit or aquifer (overburden, bedrock)	
Thickness, areal extent of water-bearing units and aquifers	
Type of porosity (primary, such as intergranular pore space, or secondary, such as bedrock discontinuities, e.g., fracture or solution cavities)	
Presence or absence of impermeable units or confining layers	
Depths to water tables; thickness of vadose zone	
Hydraulic	
Hydraulic properties of water-bearing unit or aquifer (hydraulic conductivity, transmissivity, storability, porosity, dispersivity)	
Pressure conditions (confined, unconfined, leaky confined)	
Groundwater flow directions (hydraulic gradients, both horizontal and vertical), volumes (specific discharge), rate (average linear velocity)	
Recharge and discharge areas	
Groundwater or surface water interactions; areas of groundwater discharge to surface water	
Seasonal variations of groundwater conditions	
Groundwater Use	
Existing or potential underground sources of drinking water	
Existing or near-site use of groundwater	

2.3.3 Water Use

Beginning in the 1950s when the U.S. Geological Survey began estimating water use in the United States, water supplies and uses have been influenced by several factors such as population growth, economic trends, legal decisions, and, most notably in recent years, drought. In 2000, freshwater use from surface water and groundwater sources such as rivers, lakes, reservoirs, and wells amounted to approximately 1300 billion L/day in the United States (Figure 2.13). The two primary users of this large amount of water were agriculture (34%) and the thermoelectric power industry (48%), followed by municipalities (11%), aquaculture (1%), nonmunicipal domestic (<1%), mining (<1%), livestock (<1%), and other industries (~5%) (Figure 2.14). Freshwater use was 85% surface water vs. 15% groundwater sources. Irrigation actually utilizes more freshwater (30% surface and 68% groundwater sources), whereas thermoelectric power relies heavily on saline water (35%). Although it appears that thermoelectric power production requires a large amount of water, most of the water used is for cooling purposes; the heated water is then discharged for other uses. Because our main concern in this book is with soils and environmental quality we focus primarily on agricultural, aquaculture, and livestock water use (see the Environment Quality Issues/Events Box, Tapping into the Ogallala Aquifer, p. 49).

Irrigation water use in the United States increased by about 70% from 1950 to 1980 and since has slightly decreased. Even though irrigation water use is dependent on factors such as precipitation, water availability, energy costs, farm commodity prices, application technologies, and conservation practices, the total amount of water used for irrigation actually decreased from 1980 to 2000, while the total irrigated area remained consistent at about 23.5 million ha between 1980 and 1995; currently there are approximately 25 million ha of irrigated lands, in part, due to drought. In the 17 western states, irrigated lands and water use declined during this period due to alterations in land use caused by urban growth, increased dry-land farming, and ownership of water rights shifting from agriculture to municipalities. Irrigation of lands in the western

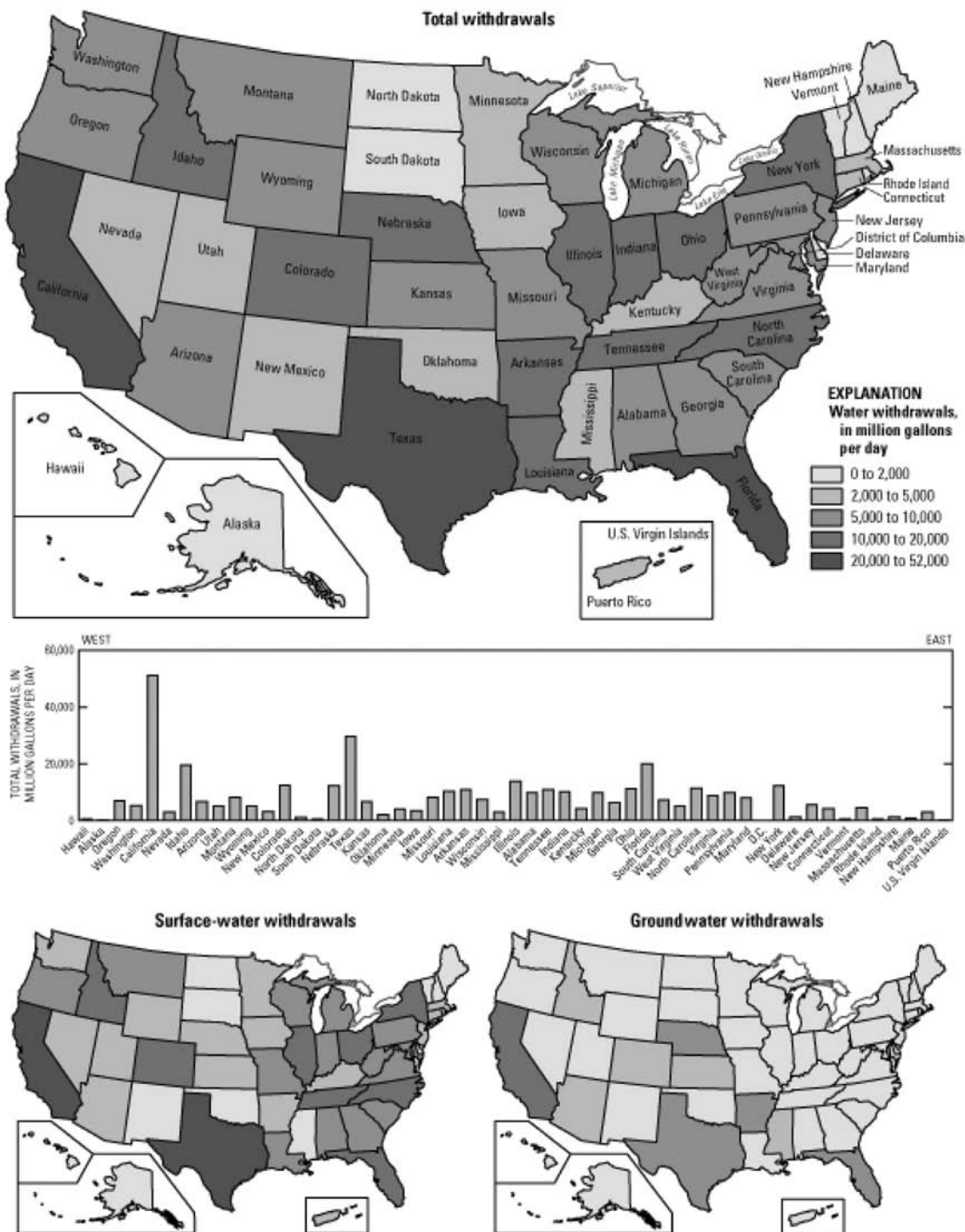


Figure 2.13 (Color figure follows p. 242.) Geographic distribution of total, surface water, and groundwater withdrawals in the United States during 2000. Note that California, Texas, and Florida accounted for 25% of total water withdrawals. California and Texas utilize 17% of the total surface-water withdrawals, whereas California alone accounts for 18% of the total groundwater withdrawals. (From Hutson, S. S. et al., Estimated Use of Water in the United States in 2000, U.S. Geological Survey. USGS Circular 1268, released March 2004, revised April 2004, May 2004.)

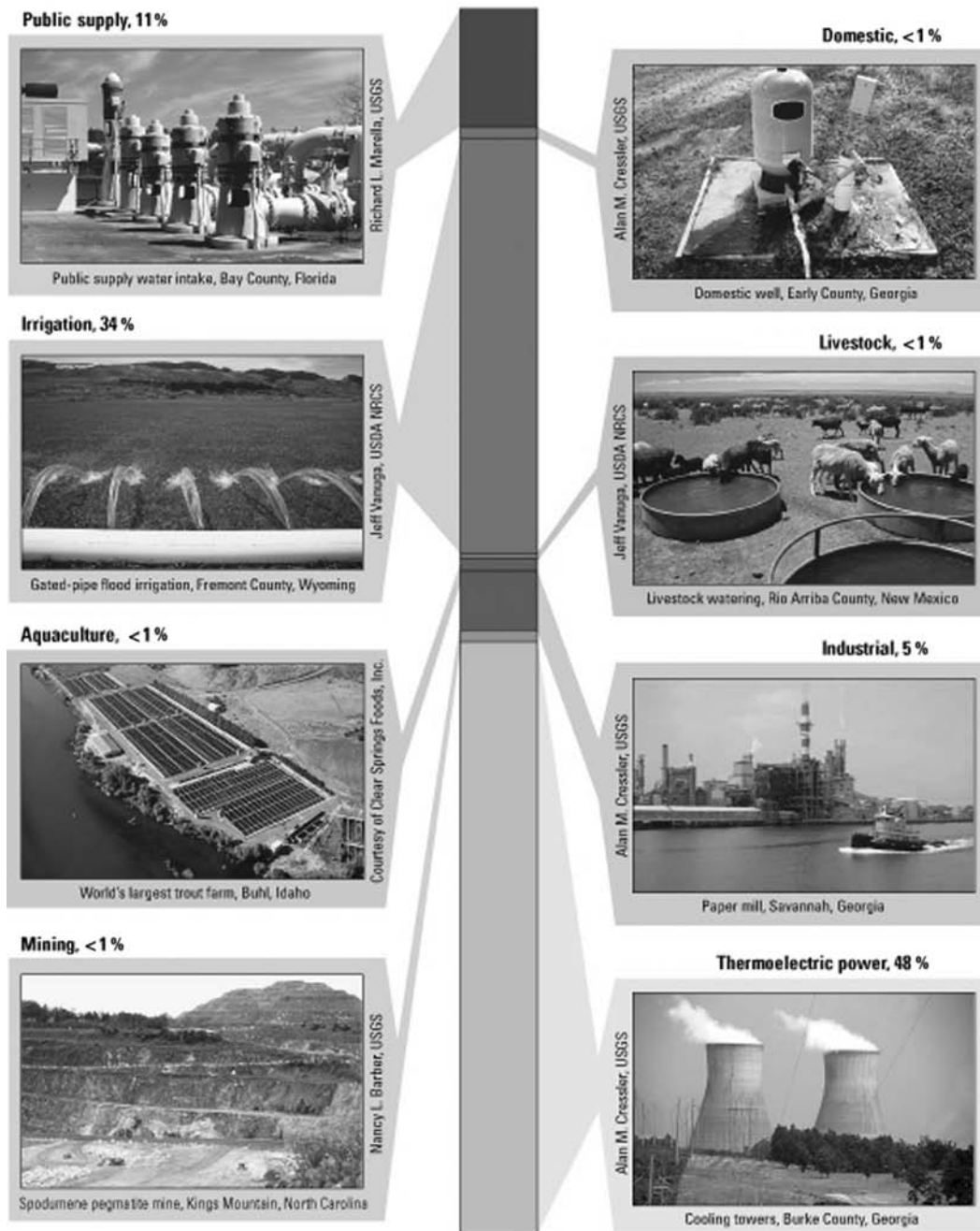


Figure 2.14 (Color figure follows p. 242.) Water use in the United States for 2000 based on estimates of water withdrawals for public supply, domestic, irrigation, livestock, aquaculture, industrial, mining, and thermoelectric power. (From Hutson, S. S. et al., Estimated Use of Water in the United States in 2000, U.S. Geological Survey. USGS Circular 1268, released March 2004, revised April 2004, May 2004.)

United States is required because of low precipitation (<50 cm), which is inadequate to sustain proper crop growth. On the other hand, there has been an increase in irrigated lands in the eastern United States during this same period. Surface water is used primarily in the arid western and mountain states and groundwater used primarily in the central states. Four states, California,

Idaho, Colorado, and Nebraska, utilize about 50% of irrigation water used; California and Idaho account for 40% of surface water irrigation use, and California and Nebraska account for about 33% of groundwater irrigation use. Water use throughout the United States today averages about 0.76 hectare-meters (i.e., 2.5 acre-feet), down from more than 1.1 hectare-meters (3.5 acre-feet) in 1950. Of the approximate 25 million ha of irrigated lands, 47, 46, and 7% used flood, sprinkler, and microirrigation, respectively. The western United States accounts for approximately 47% of the nation's total freshwater withdrawal, and with 90% of this water used for irrigation, the West accounts for about 70% of the nation's irrigation water use.

Because of their large populations and agricultural operations it is not surprising that California, Texas, and Florida are the largest consumers of water in the United States, accounting for approximately 25% of the total water use. However, most of California's water is used to irrigate 4.1 million ha, which amounts to 22% of the total U.S. irrigation water use; Nebraska (3.0 million ha) and Texas (2.6 million ha) are the states with next largest hectares of irrigated lands. It may be surprising to some that more water is used for *aquaculture* (14.0 billion L/day) than is used for livestock (6.6 billion L/day); more water is needed to raise fish than is required for cattle, poultry, and hog production. Idaho is the largest consumer of aquaculture water withdrawals at 53% of the total U.S. aquaculture water use. Most of Idaho's livestock water is used for fish farms (7.4 billion L/day) that produce about 80% of the world's *farm-raised trout*. *Catfish farming* also consumes much of our water used for livestock production. Louisiana uses 33 times more water for fish farming than is consumed in producing meat, poultry, and milk.

How much water do we use for domestic purposes? In the United States, from 200 to 750 L (average of 300 L/day) are used per person on a daily basis for such in-home activities as drinking, cooking, bathing, washing clothes and dishes, toilet flushing, and lawn and garden watering. Since 1995, the amount of municipal (85% of total U.S. population) and domestic (15%) water use has increased, primarily due to an increase in population. However, there has been a general reduction in water use per individual as there is greater public education on the awareness of water conservation practices such as use of low-flow toilets, showerheads, and faucets; *xeriscaping* (landscaping with plants that have low-water-use requirements particularly in the western United States; Lewis, 2003); and proper lawn watering to name a few. Reductions in water use result in energy and cost savings because municipalities generally charge homeowners for sewage treatment based on their domestic water consumption.

Environmental Quality Issues/Events

Tapping into the Ogallala Aquifer

Underneath much of the central and southern Great Plains states is the extensive Ogallala "High Plains" aquifer (Figure 2.15), which is one of the world's largest aquifers (450,000 km²). In 1990, it was estimated that the Ogallala contained 400 million hectare-meters of water, approximately equivalent to the amount of water in Lake Huron. The percentage of Ogallala water that resides under different states is 65, 12, 10, 4, 3.5, 2, 2, and 1.5% beneath Nebraska, Texas, Kansas, Colorado, Oklahoma, Wyoming, South Dakota, and New Mexico, respectively. The Ogallala has been the main provider of irrigation water in the agricultural region known as the "breadbasket of the world." More than 6 million ha are irrigated from the aquifer and yield a significant portion of U.S. agricultural products used for domestic human consumption (e.g., flour and cotton) and animals (e.g., feedlots), as well as for foreign exports. More Ogallala water is used annually for irrigation purposes than the entire flow of the Colorado River.

Prior to the 20th century western agricultural movement, minor amounts of Ogallala aquifer discharge occurred in playa basins and from streams, seeps, and springs located primarily along the eastern boundary of the High Plains. However, in the early 1900s, agriculture within the Ogallala region started utilizing water from the aquifer. After a slow increase in water use, the number of wells tapping into the Ogallala

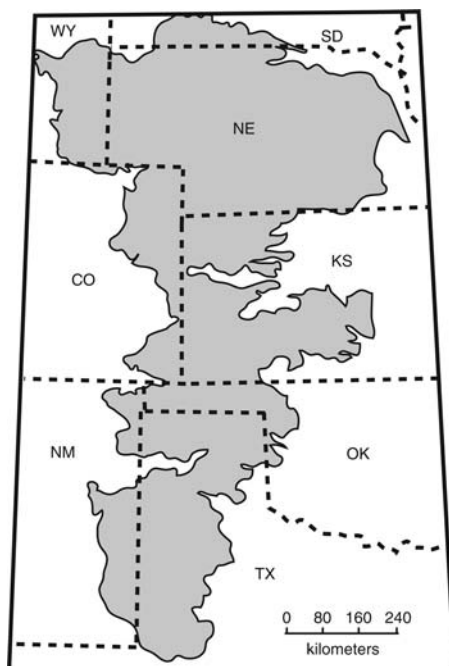


Figure 2.15 Location of the Ogallala High Plains aquifer that underlies eight states.

aquifer, and the amount of water used, increased rapidly from the mid-1940s into the 1970s. For example, in west Texas the number of irrigation wells in 1914, 1937, 1954, 1971, and 1978 was approximately 140, 1200, 28,000, 66,000, and 75,000, respectively.

Approximately 97% of the water withdrawn from the Ogallala aquifer is used for irrigation; about two thirds of U.S. irrigated land is located in the High Plains region. During the early years, there was very little consideration given to conserving water, and irrigation practices included unlined ditches and inefficient sprinkler systems. It was not unusual for these types of practices to result in less than 50% water-use efficiencies due to high evaporation rates and percolation below the rooting zone. As the number of wells tapping into the Ogallala water source increased each year, the aquifer water table increased in depth. Between 1950 and 1980, annual water use for irrigation increased from about 0.5 million to 3 million hectare-meters, although there has been a decrease in water use since the early 1980s. In some areas the water table dropped at rates of 15 to 100 cm/year; a large region in Texas and smaller areas in Kansas and Oklahoma have experienced overall declines in the water table by greater than 30 m (Figure 2.16). The consequence of a lower water table meant new wells had to be drilled deeper and some of the old wells that went dry had to be either abandoned or deepened. The increased costs associated with drilling deeper wells and the greater energy required to pump water from these lower depths caused reductions in agricultural profits with time.

Water yields from Ogallala wells have decreased over time because the water table has declined. A loss in yield results in fewer hectares that can be irrigated from a well. As an example, a well that delivers 3000 L/min can irrigate 65 ha (e.g., 160 acres, a quarter-section, or a quarter square mile) using a center-pivot irrigation system. In some parts of Texas, water yields have declined to less than 1000 L/min with the average number of hectares irrigated per well at 25 in 1980. In 1990, 30,000 million L of water/day were withdrawn from the Ogallala, of which Nebraska's consumption was 17,000 million L/day. As noted earlier, almost 97% of Ogallala water use is for irrigated agriculture.

The quality of Ogallala aquifer water is generally good with a total dissolved solids (TDS) concentration usually less than 500 mg/L. Crop production is generally not limited when irrigation waters contain 500 to 1500 mg/L dissolved solids, unless sodium (Na) is a major constituent of the dissolved substances. Ogallala waters in southern Texas have been reported to contain dissolved solids at concentrations exceeding 3000 mg/L, which requires special management practices to be used for irrigation purposes. There are also some areas where Ogallala water quality does not meet U.S. Environmental Protection Agency (EPA)

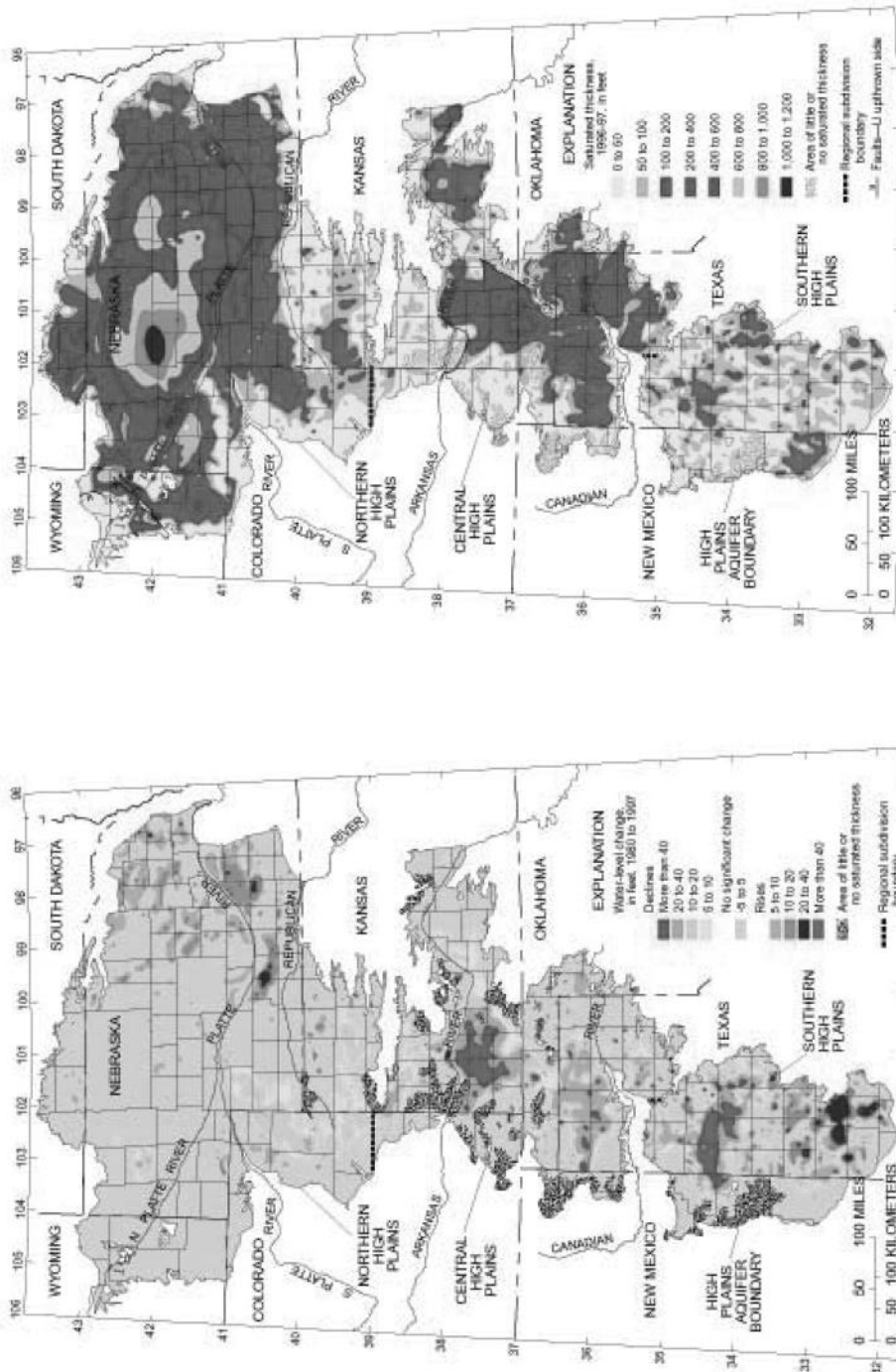


Figure 2.16

(Color figure follows p. 242.) Water level change (1980 to 1997) and saturated thickness (vertical distance between the water table and the aquifer floor) of the Ogallala aquifer in 1996–1997. Note that the aquifer is depleted in parts of northern Texas and west central Kansas, and that a large portion of the Ogallala water exists beneath the Nebraska Sandhills, which remains relatively untapped due to a lack of crop irrigation that is deemed uneconomical. (From McGuire, V. L. et al., "Water-level changes, 1980 to 1997, and saturated thickness, 1996–1997, in the high plains aquifer, U.S. Geological Survey Fact Sheet FS-124-99, Washington, D.C. Available at http://ne.water.usgs.gov/highplains/hp97_web_report/fs-124-99.htm.)

drinking water standards because of high TDS concentrations and/or high Na, Cl, sulfate (SO_4^{2-}), nitrate (NO_3^-), Se, and fluorine (F) levels. Some waters sampled in Nebraska and Kansas also contained measurable concentrations of the herbicides Atrazine and 2,4-D (2,4-dichlorophenoxyacetic acid).

Water in the Ogallala aquifer flows at a rate of about 50 m/year in a northwest to southeast direction. As water is deleted from the aquifer, there is not enough natural recharge from precipitation to compensate for the loss. At one time it was estimated that the Ogallala would be drained in the early 21st century. However, some regions have implemented conservation practices that have increased water-use efficiencies from less than 50% in the mid-1970s to 75% in 1990, and have further improved water use by installing state-of-the-art low-pressure, drip center-pivot irrigation systems that are close to 95% efficient and underground drip irrigation systems that essentially eliminate evaporative losses and are nearly 100% efficient. The U.S. Department of Agriculture (USDA) Conservation Reserve Program (CRP) has also decreased the number of irrigated hectares, particularly lands in areas that suffer from declining well yields, increased energy costs, lower farm profits, and poor water quality. This program resulted in a substantial decrease in the number of irrigated hectares; for example, there was a two thirds reduction in Texas High Plains irrigated lands between 1979 and 1989. However, with a loss of CRP funding, many of the lands enrolled in this program will again be used for irrigated agriculture purposes. In western Kansas, an Irrigation Research Project (IRP) was developed to evaluate solutions to the loss of the Ogallala water resource. The IRP will examine, evaluate, and develop (1) innovative irrigation systems; (2) profitable cultural practices; (3) economic feasibility of nontraditional crops; (4) management strategies to optimize water use; and (5) computer programs and models, in hopes of ensuring future economic stability to the region.

2.3.4 Legislative Efforts Related to Water Quality Issues

Legislation in the United States mandating efforts to identify waters that are polluted, to eliminate further discharge of pollutants, and to require actions to restore water quality dates to the 1940s (U.S. EPA, 1996; USGS, 1999). The *Clean Water Act* (CWA), enacted in 1948 as the *Water Pollution Control Act* (WPCA), and its amendments, is the main authority for all water pollution control actions at the federal level. This act established the *National Pollution Discharge Elimination System* (NPDES) permitting process to eliminate point-source pollution of the nation's navigable freshwaters. A 1993 amendment to the CWA also authorized federal legislation to regulate the land application of municipal biosolids (e.g., sewage sludge) that resulted when wastewaters were treated to remove pollutants prior to effluent discharge into surface waters. Most recently, the CWA has been used as the legal basis for lawsuits filed by a consortium of environmental groups against the EPA to force state governments to restore surface water quality. Settlement of these lawsuits has resulted in many states being required to define *total maximum daily loads* (TMDLs) of pollutants that cannot be exceeded if surface waters are to remain "fishable and swimmable."

Example Problem 2.4

The TMDL refers to the daily load of pollutants to a water body from a defined geographic area (e.g., kg pollutant entering the water body/day from a watershed or subwatershed) and does not pertain to the actual concentration of a pollutant in a water body (e.g., in mg pollutant/L). For example, TMDLs of 193 kg N/day and 13 kg P/day have been proposed for Delaware's Indian River Bay, a national estuary considered highly eutrophic due to point- and nonpoint-source pollution. With current nutrient loads to this bay estimated at 1285 kg N/day and 38 kg P/day, the required percent reduction in TMDLs would be

$$\frac{(1285 - 193) \text{ kg N/day}}{1285 \text{ kg N/day}} \times 100 = 85\% \text{ for N}$$

and

$$\frac{(38 - 13) \text{ kg P/day}}{38 \text{ kg N/day}} \times 100 = 66\% \text{ for P}$$

These percentages indicate there is an urgent need for substantial reductions in nutrient loading from all sources to meet the criteria established in the CWA.

The *Safe Drinking Water Act* (SDWA), which was enacted in 1974 and amended in 1996, was promulgated to protect drinking water supplies by legislating *maximum contaminant levels* (MCLs) above which waters are considered unsafe for human consumption, and defined enforcement standards that states are required to use for determining minimum treatments needed to improve water quality (Cech, 2003). Examples of some MCLs that may be associated with water quality issues are listed in Chapter 4 (Table 4.2).

2.3.5 Water Pollution

Groundwater quality is an issue that has generated much debate and concern and, along with surface water quality, was the primary reason the CWA was implemented (see Chapter 1). Several definitions have been proposed for groundwater contamination, but the definition by Miller (1980), which states, “Groundwater contamination is the degradation of the natural quality of groundwater as a result of man’s activities,” places the blame completely and clearly on humans and their misuse of the environment. Contamination of groundwaters occurs through the downward leaching of organic and inorganic chemicals, intentional discharge of wastes in subsurface wells, or contaminant spills of highly soluble, low-sorption organic and inorganic pollutants. Several factors can influence groundwater contamination potential including sorption, biodegradation, hydrolysis, solubility, volatilization, and climatic parameters such as precipitation and evapotranspiration.

There are several types of substances that can affect water quality. *Water pollution* can occur by a substance either directly or indirectly affecting a water system. The substances include inorganic, organic, and biological materials, of which some have a direct impact on water quality, whereas others indirectly cause chemical, physical, or biological changes (Table 2.4). Substances that can affect water quality, and which are discussed later in this book, include N, P, and S, trace elements, pesticides, acid rain, and greenhouse gases. Although suspended organic matter and sediments are generally present in most streams and lakes, these materials can cause water degradation by increasing the biological oxygen demand or decreasing light penetration by increasing water turbidity. Even changes in water temperature due to thermal discharges near industrial and power plants can alter biotic diversity in rivers and lakes. Additional water pollutants such as radionuclides, carcinogens, pathogens, and petroleum wastes are also important in the context of environmental quality but receive only limited coverage in this book. Table 2.5 lists different water pollution classes and their origins.

Table 2.4 Water Quality Parameters and Constituents

Physical Parameters	Metals and Trace Elements	Nonmetallic Constituents	Organic Chemicals	Microbiological Parameters
Conductivity	Al, Ag, As, Ca,	pH, acidity,	Methane	Coliforms
Salinity	Cd, Cr, Cu, Fe,	alkalinity,	Oil and grease	Bacteria
Sodicity	Mg, Mn, Na,	dissolved O ₂ ,	Organic acids	Viruses
Dissolved solids	Ni, Pb, Se, Sr,	B, CO ₂ , HCO ₃ ,	Volatile acids	
Temperature	Zn	Cl, CN, F, I,	Organic C	
Odors		NH ₄ , NO ₂ ,	Pesticides	
		NO ₃ , P, Si, SO ₄	Phenols	
			Surfactants	

Table 2.5 Different Classes of Water Pollutants and Their Causes

Water Pollutant Class	Contributions
Oxygen-consuming wastes	Decaying plant and animal remains, human or animal waste
Plant nutrients	N and P from fertilizers
Inorganic chemicals	Toxic metals and acidic substances from mining operations and various industrial wastes
Organic chemicals	Petroleum products, pesticides, and materials from organic wastes industrial operations
Sediments	Fine soil and sediment particles that reduce solar radiation into water bodies, reducing food production
Infectious agents	Bacteria and viruses
Radioactive substances	Waste materials from mining and processing of radioactive substances or from improper disposal of radioactive isotopes
Industrial thermal energy	Cooling waters from thermoelectric power facilities

2.3.5.1 Acidity

The *acidity* of water bodies has important consequences on the survival of aquatic organisms. Acid pH levels can be detrimental to fish, invertebrates, and other water organisms that are affected either directly or indirectly by acidic substances. For example, trace elements, e.g., aluminum (Al^{3+}), manganese (Mn^{2+}), copper (Cu^{2+}), that increase in concentration in low-pH waters can be toxic, but even high levels of H^+ ions (low pH) can result in lakes, streams, and rivers that no longer support aquatic life.

In simplest terms, acids are substances that tend to donate protons (H^+) to another substance in a chemical reaction. Acids are often classified as strong or weak, with strong acids tending to dissociate (lose H^+) completely in water and weak acids undergoing only partial dissociation. In addition to H_2SO_4 and HNO_3 , other common strong acids are hydrochloric (HCl) and phosphoric (H_3PO_4); weak acids include carbonic (H_2CO_3), acetic (CH_3COOH), and boric (H_3BO_3). (Note that only H_2SO_4 and HNO_3 are important components of acidic deposition.) The term pH is used to indicate the relative acidity of a solution (or soil) and is defined as the negative logarithm of the activity of the H^+ in solution [$\text{pH} = -\log(\text{H}^+)$]; hence, the greater the H^+ activity in a solution, the lower the pH. Pure water has a pH of 7.0, natural rainfall about 5.6, and severely acidic deposition less than 4.0. The pH of most soils ranges from 3.0 to 8.0. See Chapter 3 for more information on soil pH.

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	ACID				NEUTRAL						ALKALINE				

When acids are added to aquatic ecosystems, the decrease in pH that occurs depends greatly on the buffering capacity of the system. *Buffering* refers to the ability of a system to maintain its present pH by neutralizing added acidity. In freshwaters, the primary buffering mechanism is the reaction of dissolved bicarbonate ions with H^+ , i.e.,



and



2.3.5.2 Eutrophication

Water quality is, and will continue to be, a major economic and environmental issue. The process of eutrophication is one example of why water quality is so important. For example, excessive nutrient additions to surface waters can lead to enhanced algal growth, decreased dissolved O₂, and reduced water transparency (Table 2.6). *Eutrophication* of lakes, streams, rivers, and other surface water bodies occurs when excessive amounts of nutrients, such as N and P, are added to the ecosystem. As nutrient inputs to surface waters gradually increase, the trophic state of the water body passes through four trophic stages: *oligotrophic*, *mesotrophic*, *eutrophic*, and *hypereutrophic*. At each stage, progressive changes in the ecology of water bodies occur, usually negatively affecting their economic and recreational uses. Some water quality problems associated with eutrophication are summarized in Table 2.7. The two nutrients that are the primary concern — N and P — and their role in eutrophication are discussed extensively in Chapters 5 and 6.

2.3.5.3 Surface Runoff and Sediments

Surface runoff is a precipitation event–driven process. Runoff occurs during and shortly after the precipitation event occurs. A water sample can be collected that represents the entire volume of runoff or samples can be collected periodically during the runoff event. Specialized equipment is required for this latter collection process, which is particularly challenging because of the large volumes of water that are generated during rainfall events. For example, 1 cm of runoff over a

Table 2.6 Comparison of General Characteristics and Selected Properties of Oligotrophic and Eutrophic Water Bodies

Characteristic	Oligotrophic	Eutrophic
Nutrient status	Low	High
Algal blooms	Rare	Common
Biomass	Low	High
Aquatic diversity	High	Low
Dissolved oxygen (saturation %)	>80	<10
Total N (μg/L)	<200	>500
Total P (μg/L)	4–10	>30
Chlorophyll (mg/L)	1–3	>8
Turbidity (m) (Secchi disk transparency)	6–12	<2

Table 2.7 Water Quality Problems Associated with Eutrophication

Water Quality Problem	Contributing Factors from Eutrophication
Water safety, taste, odor	Nutrients, suspended sediments degrade water quality and increase cost and difficulty of drinking water purification; anoxic conditions and toxins produced in algal blooms can cause fish kills and make water unsafe for birds and livestock
Low species diversity	Stimulated growth of certain organisms decreases number and size of population of other species; with time, lake becomes dominated by algae and coarse, rapid-growing fish; high quality edible fish, submerged macrophytes, and benthic organisms disappear
Impairment of recreational use and navigation	Increased sedimentation decreases lake depth; enhanced vegetative growth blocks navigable waterways; decaying algal biomass produces surface scums and odors, and increases populations of insect pests

hectare of land will result in a volume of 100,000 L. When runoff is collected from large areas, small flow-weighted samples are gathered that represent the entire volume of water.

Sediment loading to surface water bodies is a major water quality problem due to siltation and the potential nutrients, pesticides, and organic matter adsorbed to these materials. Other physical concerns related to increased particulate introduction are decreased light penetration from increased turbidity that reduces the growth of benthic plants and the buildup of materials due to sediment deposition that results in a loss of water-storage capacity in reservoirs, lakes, and wetlands.

Surface runoff and eroded materials that enter water bodies usually result in a reduction in water quality. The concentration of soluble materials in surface runoff is generally a function of their solubility. Concentrations of contaminants in the transported soil-sorbed chemicals in overland flow, however, are usually greater than the bulk soil source concentrations. To determine the importance of sorbed chemicals in the eroding sediments, an *enrichment ratio* (ER) can be calculated that describes the ratio of the concentration of the chemical in the eroded material to that in the bulk soil:

$$ER = \frac{\text{mg chemical/kg eroded soil}}{\text{mg chemical/kg bulk soil}} \quad (2.3)$$

Values for ER are generally greater than 1 and are dependent on soil type, erosion mechanism, and total mass of soil eroded. Organic matter and fine clay particles have greater surface areas and adsorption capacities. Erosion of these materials would usually result in higher ER values. Rainfall detachment processes are also responsible for producing higher values of ER than simple sediment detachment from surface runoff, primarily because rainfall detachment results in smaller particles. Over time, a constant erosion event will produce sediments that have larger values of ER at the initial stages of precipitation that then taper off to ER values closer to 1 in the later stages of the event.

The *runoff coefficient* (RC) is also used to characterize surface runoff:

$$RC = \frac{\text{volume of runoff/unit area}}{\text{volume of rainfall/unit area}} \quad (2.4)$$

The RC is most often used for a single storm event and expresses the fraction (or percent) of the precipitation that leaves the area through overland flow. An area with an impermeable surface such as a parking lot obviously has little infiltration potential and would have an RC near 100%, whereas a freshly tilled field would have an RC less than 5%. The RC is influenced by many factors including the inherent infiltration rate of the soil, the slope, rainfall intensity, and antecedent moisture conditions. The total amount of sediment or contaminant leaving an area is a product of the volume of water leaving as overland flow and the concentration of sediment or contaminant in the water.

2.3.5.4 Water Quality

Water contaminants include inorganic, organic, and biological materials, some of which have a direct impact on water quality, others of which indirectly cause physical, chemical, or biological changes. Substances that can affect groundwaters include nutrients, salts, heavy metals, trace elements, and organic chemicals, as well as contaminants such as radionuclides, carcinogens, pathogens, and petroleum wastes (see Table 2.4). Organic contamination may result from leaking gas tanks, oil spills, or runoff from equipment-servicing areas. In these cases, the source of the contamination must be identified and removed. Gasoline, diesel, or oil-soaked areas should be immediately excavated and disposed of by approved methods.

The chemistry of groundwaters and potential levels of naturally occurring contaminants are related to (1) groundwater hydrologic conditions, (2) mineralogy of locally impacted geological

material, (3) extent of disturbed materials and its exposure to atmospheric conditions, and (4) time. Movement of metal contaminants in groundwater varies depending on the chemical of concern, and include considerations such as with cobalt (Co), Cu, nickel (Ni) and zinc (Zn) mobility being greater than silver (Ag) and Pb, which tend to be more mobile than Au and Sn. As conditions such as pH, redox, and ionic strength change over time, dissolved constituents in both surface waters and groundwaters may decrease due to adsorption, precipitation, and chemical speciation reactions and transformations.

When organic matter such as municipal biosolids and animal manures are added to surface waters, a rapid decline in available O_2 can occur. Oxygen is consumed in the biological decomposition of the added organic matter, and by oxidation of other reduced inorganic compounds, i.e., ammonium (NH_4^+), ferrous iron (Fe^{2+}), and sulfite (SO_3^{2-}), present in the added material. This results in lower O_2 availability for higher forms of aquatic life. Two measures that are used to estimate the quality of surface waters are *biochemical (or biological) oxygen demand* (BOD) and *chemical oxygen demand* (COD). BOD is a measure of the amount of O_2 consumed by microorganisms over a 5-day period, whereas COD indicates how much oxidizable material there is in a water sample by its chemical reaction with dichromate (Cr_2O_7). Values for COD are often higher than BOD, depending on the nature and quantity of oxidizable material in the water sample.

Biological communities (fish, plants, microorganisms, etc.) in surface waters are also affected by conditions that are influenced by pH and salt concentrations. Mining activities can have a considerable effect on the quality of both groundwaters (Vance and Skousen, 2003) and surface waters (Skousen and Vance, 2003), as well as the land and air in the surrounding environment. Oxidation of reduced S substances can lead to acid mine drainage, which can be deleterious to plants, animals, and microorganisms. Acid mine drainage and some irrigation flow-through waters can also increase surface water salinity. Refer to Chapter 7 for more information on the effects of mining and Chapter 10 on organic chemicals.

Environmental Quality Issues/Events

Mining and Water Contamination

Surface and underground mining activities can have direct and indirect impacts on the quantity, quality, and usability of both surface water and groundwater supplies. The nature of the mining activity, geological substrata, and redistribution of surface and subsurface materials will determine to a large degree how water supplies will be affected. As waters interact and alter the disturbed geologic materials, constituents such as salts, metals, trace elements, and organic compounds become mobilized. Once mobilized, the dissolved substances can leach into deep aquifers, resulting in groundwater quality impacts. In addition to concerns regarding naturally occurring contaminants, mining activities may also contribute to water pollution from leaking underground storage tanks, improper disposal of lubricants and solvents, contaminant spills, as well as others.

Because mining activities can result in poor-quality waters, enforcement of regulations is needed to minimize or eliminate potential problems. The *Surface Mining Control and Reclamation Act* (SMCRA) of 1977 specifies policies and practices for mining and reclamation to minimize water quality impacts, and requires that specific actions be taken to protect the quantity and quality of both onsite and offsite water resources. All mines are required to meet either state or federal water quality guidelines, which are generally related to priority pollutant standards described in the CWA.

Acid mine drainage (AMD) is most prevalent at inactive and abandoned surface and underground mines. If geological substrata containing reduced S minerals (e.g., pyrite, FeS_2) are exposed to O_2 , such as when pyritic overburden materials are brought to the Earth's surface during mining activities and then reburied, high concentrations of sulfuric acid (H_2SO_4) can develop and form acid waters with pH levels below 2. Neutralization of some of the acidity produced during the oxidation of reduced S compounds

occurs when silicate minerals dissolve; however, during this process high levels of potentially toxic metals, such as Al, Cu, Cd, Fe, Mn, Ni, Pb, Zn, may be released. For example, mining of coal in the *Toms Run area* of northwestern Pennsylvania resulted in groundwater contamination by AMD containing high concentrations of Fe and SO_4 that leached into the underlying aquifer through joints, fractures, and abandoned oil and gas wells.

The *Gwennap Mining District* in the United Kingdom contained numerous mines that operated over several centuries to extract various mineral resources. One of these mines, the *Wheal Jane metalliferous mine* in Cornwall, extracted ores that included cassiterite (Sn-containing mineral), chalcopyrite (Cu), pyrite (Fe), wolframite (tungsten, W), arsenopyrite (arsenic, As), in addition to smaller deposits of Ag, galena (Pb), and other minerals. After closure in the early 1990s, extensive voids remaining in the Wheal Jane mine that contained oxidized and weathered minerals were flooded. Initial groundwater quality was poor with a pH of 2.8 and a total metal concentration close to 5000 mg/L, which contained high levels of Fe, Zn, Cu, and Cd. Water quality worsened with depth, and at 180 m the groundwater had a pH of 2.5 and metal concentrations of 2200, 1500, 44, and 5 mg/L for Fe, Zn, Cu, and Cd, respectively. Current treatment of discharge waters originating from the mine involves an expensive process and will continue to be long term if environment quality in the region is to be preserved. A similar situation occurred when a Zn mine in southwestern France was closed. After flooding, discharge mine waters contained high concentrations of Zn, Cd, Mn, Fe, and SO_4 even though the solution pH was near neutral.

Within the *Coeur D'Alene District of Idaho*, location of the *Bunker Hill Superfund site*, groundwater samples have been found to contain high concentrations of Zn, Pb, and Cd. The contamination was believed to originate from the leaching of old mine tailings that were deposited on a sand and gravel aquifer. When settling ponds were developed nearby the old tailings, recharge of the local groundwaters resulted in a rise in the water table that saturated the tailings causing considerable metal leaching to occur.

Gold mining operations have used cyanide as a leaching agent to solubilize Au from ores, which often contain arsenopyrite (As, Fe, S), and in some cases pyrite. During the leaching process, Ag is also recovered as a by-product if present. Unfortunately, cyanide is a powerful, nonselective solvent that will solubilize numerous substances that can be environmental contaminants. These ore waste materials are often stored in tailing ponds, and depending on the local geology and climate, cyanide present in the tailings can exist as free cyanide (CN^- , HCN), inorganic compounds (NaCN , HgCN_2), metal-cyanide complexes with Cu, Fe, Ni, and Zn, or the compound CNS. Because cyanide species are mobile and persistent under certain conditions, there is the potential for trace element and cyanide migration into groundwaters. For example, a tailings dam failure resulted in cyanide contamination of groundwater at a gold mining operation in British Columbia, Canada.

Arsenic and uranium (U) contamination has resulted from extensive mining and smelting of ores containing various metals (Ag, Au, Co, Ni, Pb, and Zn) and/or nonmetals (As, P, and U). Contaminated As groundwaters have been a source of surface recharge and drinking water supplies; levels of As in a contaminated river of Canada were 7 and 13 times greater than the recommended national and local drinking water standards, respectively. Arsenic is known as a carcinogen and has been the contributing cause of death to humans in several parts of the world that rely on As-contaminated drinking waters. Waters from dewatering a uranium mine in New Mexico had elevated levels of U and radium (Ra) activities as well as high concentrations of dissolved molybdenum (Mo) and Se, which were detected in stream waters 140 km downstream from the mine.

Mine sites that have been contaminated generally contain mixtures of inorganic and organic constituents, so it is important to understand these multicomponent systems in order to develop remediation strategies. Therefore, a proper remediation program must consider *identification*, *assessment*, and *correction* of the problem. *Identification* of a potential problem site requires that either the past history of the area and activities that took place be known or that a water analysis has indicated that a site has been contaminated. *Assessment* addresses questions such as is there a problem, where is the problem, and what is the extent of the problem? Afterward, a *remediation action* plan must be developed that will address the specific problems identified. A remediation action program may require that substrata materials (e.g., backfill) and groundwater be treated. More information can be found in Chapter 12, Remediation of Soil and Groundwater, and Chapter 13, Risk Assessment.

PROBLEMS

- 2.1 Explain how the biosphere is related to the atmosphere and hydrosphere. Provide examples of how changes in environmental quality, i.e., global climate change, water pollution, etc., may affect different biological species such as trees, fish, and deer populations and habitat migration.
- 2.2 Although the troposphere is primarily responsible for weather conditions that we experience on a daily, seasonal, and yearly basis, what other properties and influences are important in the role of climate?
- 2.3 Write an equation that demonstrates how calcite (CaCO_3) formation in soils removes CO_2 from the atmosphere. Where would soils with appreciable amounts of CaCO_3 be found?
- 2.4 Which of the tropospheric gases is the most variable and why? Explain why atmospheric oxygen (O_2) is more important to humans than atmospheric nitrogen (N_2).
- 2.5 How important is the atmosphere in the cycling of pollutants? What kinds of materials are more susceptible to long-range transport and deposition? Why do you think gases trapped in polar ice are important to the study of environmental quality?
- 2.6 Select three cities, one each from the West Coast, the mid-continent, and the East Coast, and track their weather conditions (e.g., high and low temperatures, precipitation, and any other weather-related conditions) for a week. Describe the changes that occurred during the weekly evaluation and provide reasons for these variations. You can find temperature and precipitation data on Web sites on the Internet.
- 2.7 Explain why topography can influence vegetative communities. Be sure to include a discussion of how slope aspect (e.g., south- vs. north-facing slopes) modifies the microclimatic (e.g., local temperature, winds, rainfall) and soil (e.g., moisture, temperature, organic matter content) conditions that affect vegetation dynamics.
- 2.8 Use the data provided in Figure 2.6 and determine the approximate amount and relative proportion of precipitation that occurs in the three cities during the winter (December, January, February), spring (March, April, May), summer (June, July, August), and autumn (September, October, November) seasons.
- 2.9 What would happen if ice (solid phase) had a density higher than water (liquid phase)? Think of aquatic ecosystems and the impacts that would occur if surface ice were to sink to lake and river bottoms or if these environments froze from the bottom up.
- 2.10 Calculate the MRT and pollution potential for a contaminant in a pond that has a volume of 0.1 km^3 , an outlet flow rate of $2 \text{ m}^3/\text{s}$, and an inorganic contaminant (1 kg) that is highly soluble and toxic to fish. Compare your answer to a lake with a volume of 0.5 km^3 and a flow rate of $50 \text{ m}^3/\text{s}$, with 10 kg of the same contaminant.
- 2.11 Provide some examples of conservation methods that could decrease water use by (a) the homeowner, (b) irrigated agricultural sector, (c) city parks and recreational departments, and (d) golf course operations.
- 2.12 What impacts could urbanization have on the water quality of a river that flows through the development? How do cities prevent the contamination of their drinking water sources? Are water pollution problems always associated with human activities?
- 2.13 The enrichment ratio for N [$\text{ER}_{(\text{N})}$] in a 10-ha agricultural area is 4 during a storm event. Assuming the total soil N concentration is 1200 mg/kg , how much N would be added to the stream if the storm resulted in erosion of 1 Mg soil/ha from the field? If the farmer implements a conservation practice that reduces the amount of erosion by 50%, determine the reduction in the amount of N entering the stream considering a similar type of storm event.
- 2.14 Runoff is collected from small plots $2 \times 2 \text{ m}$ in size. A thunderstorm delivers 5 cm of rain and 30 L of runoff is collected. Calculate the RC.
- 2.15 Runoff is collected from an area 1 ha in size. The soil in this small watershed contains 600 mg/kg total P. A storm delivers 2.5 cm of rain and the runoff collector device indicates $50,000 \text{ L}$ of runoff was generated. A representative sample of the runoff has 6000 mg/L of sediment and the sediment contains 1000 mg P/kg . Calculate the RC, enrichment ratio for P, the amount of sediment lost (in kg sediment/ha), and the amount of sediment-bound P lost (in kg P/ha).
- 2.16 Explain the difference between a TMDL and an MCL. What is the value of establishing TMDLs for use in watershed-scale water quality protection efforts?

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Our Environment: Soil Ecosystems

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3.1 INTRODUCTION

The term *soil* has different meanings to individuals depending on their scientific background and experience. For example, to the agronomist or botanist soil is best defined as a medium for plant growth, to the engineer soil refers to the loose material that lies between the ground surface and solid rock, and to the soil scientist soil is defined as the unconsolidated mineral and organic matter at the Earth's surface that has been altered by *pedogenetic* (soil-forming) processes. Although there is no uniform, comprehensive definition for soil, it is apparent that the functions of soil are numerous. Soils are dynamic ecosystems that support plant life by providing the essential requirements for plant growth, including nutrients, water (H₂O), oxygen (O₂), and support. Soil is also necessary to sustain human life because it provides natural resources (e.g., food, fiber, construction materials), support for dwellings and roads, and a means of recycling or detoxifying waste materials that are produced daily. Because soils are so important to human populations and environmental quality, it is imperative that we appreciate soil characteristics, properties, functions, and how soils should be managed to maintain sustainable environments.

Various physical, chemical, and biological processes have resulted in the development of soils over geologic time. The following sections on the soil environment delineate the important features and define the terms commonly used to characterize soils. To categorize soils for land-use purposes, it is necessary to understand the general properties of soils, as well as how to qualify and quantify select physical, chemical, and biological factors important to soil health and land management. In addition to gaining a better understanding of soil properties and characteristics, we should also know the specific components of a successful testing program for air, soil, plants, water, and by-products that apply to land-use programs involving plant growth, crop yields, by-product utilization, soil amendments, and contaminant concentrations of interest in any media. A sound testing program is critical for both the agronomic and environmental perspective. Important considerations and approaches to consider in testing programs are included in Chapter 4 on environmental testing. Chapters 2 and 3 are critical to the evaluation of specific considerations related to soil, water, and air testing where protection of human health and environmental quality are primary concerns.

3.2 THE SOIL ENVIRONMENT

Soils are defined according to Singer and Munns (2002) as:

Complex biogeochemical materials on which plants may grow; having structural and biological properties that distinguish them from the rock and sediments from which they normally originate; consisting of dynamic ecological systems that provide plants with support, water, nutrients, and air; supporting all ecosystems on land including a large population of microorganisms that recycle the materials of life; sustaining the entire human population with food, fiber, water, building materials, and sites for construction and waste disposal; and protecting ground water by filtering toxic chemicals and disease organisms from waste water.

Thus, soils and soil materials are used for agricultural, engineering, environmental, and other important functions. For the purpose of this book, soil is defined as *a natural, three-dimensional array of vertically differentiated material at the surface of the Earth's crust*. The variation in soils throughout the world is a function (f) of *five soil-forming factors* (Jenny, 1941), which can be expressed as:

$$\text{Soil} = f(pm, r, cl, o, t) \quad (3.1)$$

with pm , r , cl , o , and t representing parent material, relief (topography), climate, organisms, and time, respectively. Equation 3.1 indicates that the formation of a particular soil is determined by the amount of time a parent material located on a specific landscape has been affected by climate and organisms. Soil genesis is the process in which soil develops from parent materials and includes the physical and chemical weathering of parent material particles, physical movement of the particles, mineral alterations and transformations, addition of organic matter, and formation of horizons. Soils vary in horizon type and thickness, texture, structure, color, and other physical, chemical, and biological qualities and attributes.

Some of the more common agricultural uses of soil include croplands, grazing lands, pastures, forests, and various horticultural purposes. Nonagricultural uses of soils involve recreation, road and building foundations, construction materials, and waste disposal. Within the continental United States, lands (in millions of hectares) are divided approximately into 31% *grasslands, pastures, and rangelands* (234), 29% *forests* (224), 24% *croplands* (184), 6% *urban and rural residential areas* (47), and 10% *miscellaneous other lands* (78). Overall, 62% of the continental United States is used for agriculture, which includes croplands, grazing lands (pastures, range, and forests), and farmsteads with the remaining 38% of the land classified as nonagricultural (e.g., forests, transportation, recreation, defense, urban, etc.). With the increase in urbanization, some of the most productive lands, those classified as prime farmlands, have been converted to nonagricultural uses. Over the past 20 years, an annual rate of about 0.5 million ha of rural lands were used for urban development, of which about 25% were prime farmlands. With the increasing loss of our most productive soils, we are faced with using less productive lands to produce foods required by animals and humans. Land-use planning efforts that determine where we can best locate subdivisions, produce crops, and dispose of our wastes are becoming important to sustaining a balanced and sustainable environment.

Contamination of our land occurs when high enough quantities of unwanted and potentially toxic substances are intentionally disposed of, or accumulated, on site to a level that is greater than the soil's normal or background concentration (see Chapter 1 for a description of contaminated vs. polluted). Soil pollution results from chemical and biological contamination, such as contaminant spills, or the use of excessive amounts of pesticides and fertilizers that can result in surface water or groundwater contamination that can cause harm to indigenous organisms or plant life. In addition, there are other forms of soil pollution or degradation including erosion, compaction, and salinization. Soils have often been damaged when used for on-site land disposal of waste chemicals and unwanted materials (see Chapter 12 for more information on remediation of contaminated soils and groundwaters). Most soils are capable, to some degree, of sorbing and neutralizing many contaminants and pollutants to harmless levels through chemical (*abiotic*) and biochemical (*biotic*) processes. However, there are limits to the ability of a soil to accept wastes and by-products without some negative effect on the environment. To appreciate the use of our soil resources, we must understand the basic properties of soils and how they interact to regulate the health and quality of our lands.

3.3 SOIL PHYSICAL ATTRIBUTES AND PROCESSES

Soils contain solids, liquids, and gases. Soil physical characteristics and properties that are of primary interest include the composition and arrangement of solids and how movement of liquids and gases is affected by these materials. The arrangement of soil solids determines the amount of

open volume, or pore space, that a soil possesses. Organic matter contributes to darker soil colors and can significantly influence a soil's infiltration rate, water-holding capacity, permeability, aggregate stability, and consistence, even though soils contain much lower contents of organic matter than mineral materials. In this section we discuss the nature of soil physical properties and their importance in processes involving movement of soil solutions and soil gases, soil temperature, and contaminant movement in soils. Migration of soluble and gaseous pollutants is controlled to a large extent by soil physical properties.

3.3.1 Soil Physical Properties

Environmental quality is influenced to a large degree by soil physical properties. How soils function within the landscape can be determined by their ability to allow water and gas movement, which is influenced by soil texture, aspect (i.e., slope direction), and landscape position (i.e., upland, midslope, toeslope). *Parent materials* of soils are composed of mineral and organic materials that are chemically, physically, and biologically weathered. The parent materials are classified as either residual or transported materials. *Residual parent materials* are formed from the weathering of confined rocks and consist of igneous, sedimentary, and metamorphic rocks that vary in hardness, color, mineralogy, particle size, and crystallinity. *Transported parent materials* have been carried by wind or water; examples of these materials include eolian deposits of windblown sand, silt, and clay. Rapidly moving water or slowly moving glaciers are both capable of transporting large amounts of materials. *Water-transported materials* are generally sorted by particle size, whereas glacial deposits, known as till, are often mixtures of different particle sizes.

Table 3.1 Size Classification of Soil Particles According to the U.S. Department of Agriculture System

Soil Particles	Diameter (mm)	Comparison
Coarse Fragments		
Stones	>254	>10 in.
Cobbles	75–254	3–10 in.
Gravel	2–75	0.08–3 in.
Soil Particles		
Sand	2.0–0.05	
Very coarse	2.0–1.0	Thickness of a nickel
Coarse	1.0–0.5	Size of pencil lead
Medium	0.5–0.25	Salt crystal
Fine	0.25–0.10	Flat side of a book page
Very Fine	0.10–0.05	Nearly invisible to the eye
Silt	0.05–0.002	
Coarse	0.05–0.02	Root hair
Medium	0.02–0.01	Nematode
Fine	0.01–0.002	Fungi
Clay	<0.002	
Coarse	0.002–0.0002	Bacteria
Fine	<0.0002	Viruses

3.3.1.1 Particle Size and Soil Textural Classes

Soils are composed of solid materials ranging in size from stones to fine clays (Table 3.1). The larger materials, called coarse or mineral fragments, including stones, cobbles, and gravels, are chemically and physically weathered over long periods of time to form the smaller soil particles of sand, silt, and clay. Soil particles are defined on the basis of their diameter, although these particles rarely exist as spherical objects. *Clay minerals*, for example, are three-dimensional, layered structures that commonly have a platelike appearance. Soil particle sizes often differ between classification schemes used by different groups; the U.S. Department of Agriculture system (Soil Survey Staff, 1999; 2004) is used throughout this book.

There are 12 *soil textural classes* that are defined by the relative proportion of sand, silt, and clay that makes up a soil sample (Figure 3.1). There are two generally used methods for determining soil texture: (1) the field method done by hand and (2) mechanical analysis. The field method is taught in introductory soil science courses and is not discussed here. Using the mechanical analysis method to determine the sand, silt, and clay requires the removal of coarse fragments by sieving the soil through a 2-mm sieve. Chemical treatments are also necessary to remove cementing agents such as organic matter and carbonates. The sand, silt, and clay percentages should always total 100%, and once known, the soil texture can be found by using the *textural triangle* (Figure 3.1).

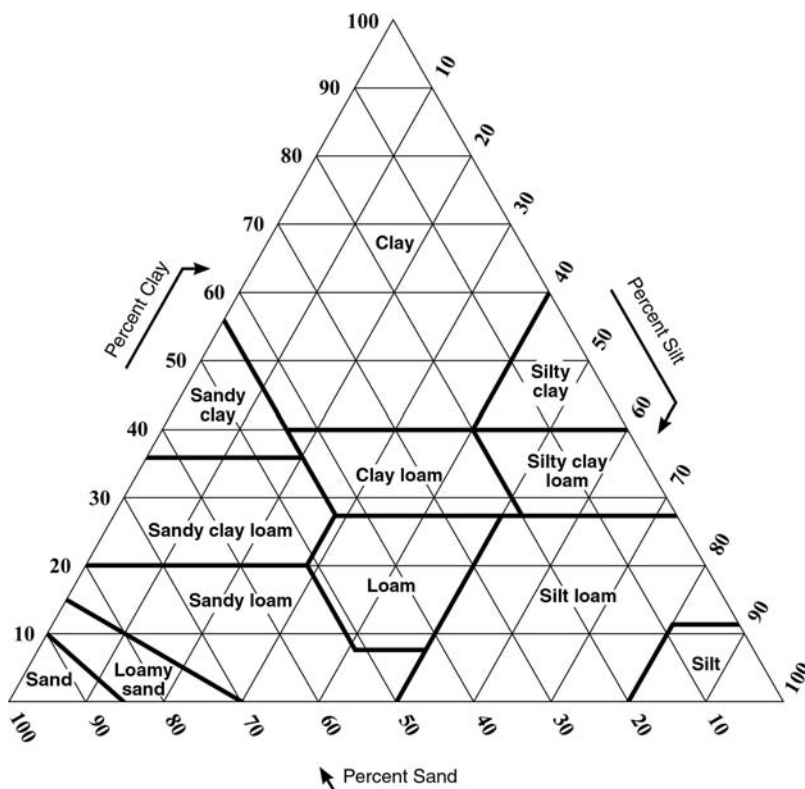


Figure 3.1 Textural triangle indicating the range in sand, silt, and clay composition for each soil textural class. The three corners of the triangle represent 100% of the primary soil particle-size classes. Note that a soil sample containing equal parts of sand, silt, and clay would be classified as a clay loam.

Example Problem 3.1

What is the textural class of a soil that contains:

40% sand + 40% silt + 20% clay?

From the textural triangle, this soil would be classified as a loam. Only two of the soil particle percentages are actually needed to determine the soil textural class because the point at which the two meet on the textural triangle determines the third soil particle percentage.

Soil texture is considered a basic property of the soil because the textural class of a particular soil generally remains unchanged over time equivalent to the human lifespan. This is one reason soil descriptions used in soil surveys (see Section 3.6) record the soil textural class of each horizon. However, a disturbance of an area, such as water or wind erosion, could alter the textural class of the soil surface of both the soil being eroded and the soil where the erosional deposition occurs. Over long time periods (geologic time), weathering and translocation of soil materials can change soil texture.

3.3.1.2 Aggregates and Soil Structure

Soil particles that are held together by chemical and physical forces form stable aggregates. Natural aggregates are called *peds*. Collectively, the type of soil aggregates or peds defines soil structure. Soil structure (Figure 3.2) influences the amount of water that enters a soil (infiltration)

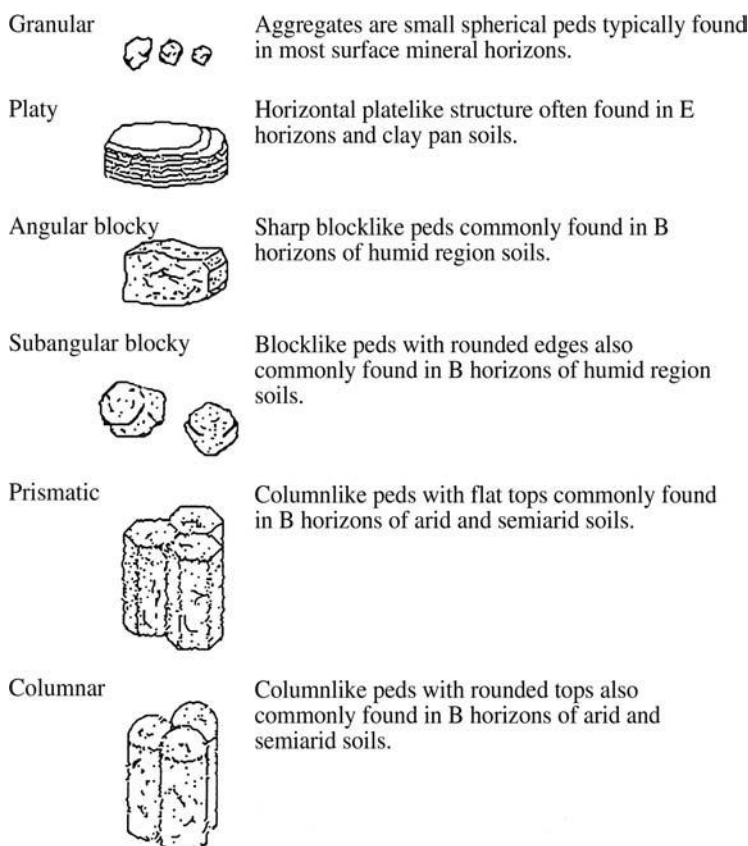


Figure 3.2 Soil structural types, descriptions, and their location in the soil profile.

and gas diffusion at the soil surface. Soil structure also plays an important role in the movement of liquid and gaseous substances through soils. The porosity of a soil is a function of its structure.

Soil structure is classified based on type, size, and grade. Common structure types include granular, platy, subangular and angular blocky, prismatic, and columnar shapes (Figure 3.2). Granular structure is representative of surface horizons. Platy structure, although not very common, is found in leached subsurface horizons of forest soils or in some clay-compacted horizons. The blocky, prismatic, and columnar structures are often found in subsurface horizons; angular and subangular blocky structures are typical of soils in humid regions, and prismatic and columnar structures are common to soils in arid and semiarid regions. Structural size classes vary with the type of structure considered, and range from very fine to very coarse. Structural grade is determined by observing the soil structure in place in a soil pit and is related to the overall structural development of a soil. Structural grades include weak, moderate, and strong classifications.

3.3.1.3 Soil Density

Particle and bulk density measurements are useful for estimating the type of soil minerals present and the degree of soil compaction, respectively. Particle density is the mass of a particle per volume (Mg/m^3 or g/cm^3); the volume of pore space and weight of water are not included in particle density measurements. Common soil minerals (quartz, feldspars, micas, and clay minerals) have particle densities between 2.60 and 2.75 Mg/m^3 , and a value often used to represent the average soil particle density is 2.65 Mg/m^3 . Bulk density is a measure of the mass per volume (Mg/m^3) of a soil. Undisturbed soils are usually used for bulk density measurements so that a true representation of the amount of solid present in a particular soil volume can be calculated; with disturbed soils, natural soil pore spaces are destroyed. Bulk density is calculated on an oven-dry weight basis and does not take into consideration the amount of water present in the soil at the time of sampling. Mineral soils, unless developed in volcanic ash, generally have bulk densities greater than 1.0 Mg/m^3 with a common bulk density of a soil with a loam texture being 1.3 Mg/m^3 . Soils with high densities (e.g., 2.0 Mg/m^3) will likely have slow water infiltration and permeability, which can result in ponding or surface runoff, and cause a reduction in plant root growth and limited gas (O_2) flux. Organic soils typically have bulk densities less than 1.0 Mg/m^3 , whereas mineral soils derived from volcanic ash often have bulk densities in the range of 0.3 to 0.85 Mg/m^3 .

3.3.1.4 Soil Solids

Soil minerals are classified as primary and secondary minerals according to their origin. Primary minerals are those that formed during the cooling of molten rock and are predominately silicate minerals (Table 3.2). Igneous rocks are composed entirely of primary minerals; metamorphic and sedimentary rocks can contain various amounts of primary and secondary minerals. Secondary minerals are formed in soils from soluble products derived from the weathering of rocks. Clay minerals, among the most important soil secondary minerals because of their large surface area and reactivity with ionic and dissolved inorganic and organic compounds, are discussed in more detail in the following sections. Carbonates and sulfates accumulate in subsoil horizons and are often the dominant secondary minerals present in soils in arid and semiarid regions.

3.3.1.5 Soil Organic and Inorganic Carbon

Carbon (C) is present in all soils in the form of soil organic matter; however, soils formed in arid regions can contain significant amounts of inorganic C as carbonate minerals. *Soil*

Table 3.2 Common Primary and Secondary Minerals Found in Soils

Mineral	Chemical Formula	Weatherability
Primary Minerals		
Quartz	SiO_2	Most resistant
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	↑
Microcline	KAlSi_3O_8	
Orthoclase	KAlSi_3O_8	↓
Biotite	$\text{KAl}(\text{Mg}, \text{Fe})_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	
Albite	$\text{NaAlSi}_3\text{O}_8$	
Hornblende	$\text{Ca}_2\text{Al}_2\text{Mg}_2\text{Fe}_3\text{Si}_6\text{O}_{22}(\text{OH})_2$	
Augite	$\text{Ca}_2(\text{Al}, \text{Fe})_4(\text{Mg}, \text{Fe})_4\text{Si}_6\text{O}_{24}$	
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	
Olivine	$(\text{Mg}, \text{Fe})_2\text{SiO}_4$	Least resistant
Secondary Minerals		
Goethite	FeOOH	Most resistant
Hematite	Fe_2O_3	↑
Gibbsite	$\text{Al}(\text{OH})_3$	
Clay minerals	Aluminosilicates	↓
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	
Calcite	CaCO_3	
Gypsum	$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	Least resistant

Source: Brady, N. C. and R. R. Weil. 2004. *Elements of the Nature and Properties of Soil*, 2nd ed., Prentice Hall, Upper Saddle River, NJ.

organic matter contents vary from less than 1% in coarse-textured soils and soils of arid regions, to nearly 100% in some poorly drained organic soils. Typical farmland topsoils may contain 2 to 10% organic matter. Organic matter influences soil physical, chemical, and biological properties. Soil structure is often improved with the addition of organic materials such as animal manures, municipal biosolids, composts, and from crop residues that are returned to the soil. *Soil inorganic carbon* includes the solid-phase carbonate minerals as well as the soluble carbonate species — carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) that are important in buffering calcareous soil systems. Further discussion on the role of soil organic C is presented in Section 3.4.1.2.

3.3.1.6 Soil Water

Soils hold water in pore spaces by the cohesive and adhesive nature of water and soil particle surfaces. *Cohesion forces* are the result of water molecule polarity and hydrogen bonding, which attracts water molecules to one another. *Adhesion forces* are responsible for attracting water molecules to soil mineral and organic matter surfaces. These forces allow water to move upward in soils by capillary action, or along surfaces of soil particles as water-films.

Several terms are used to describe soil water, including water content and water potential. Water content is a measure of the amount of water in a soil, and is usually expressed on a percent basis. The water content of a soil is determined by measuring the weight of both the water and solid materials contained in a soil sample. Each of these weights can easily be determined in the laboratory using an oven and balance.

Example Problem 3.2

The percent soil water content (SWC) is calculated as follows:

$$\%SWC = [(wet\ soil\ wt - oven-dried\ soil\ wt)/(oven-dried\ soil\ wt)] \times 100$$

For a soil with a wet weight of 160 g and a dry weight of 120 g, the %SWC would be

$$\%SWC = [(160\ g - 120\ g) / 120] \times 100 = 33.3\%$$

Soil water potential is a measure of the strength, or energy, with which water is held by the soil. Water moves in soils from areas of high water potential to low water potential; water potential is in turn related to soil moisture content, textural class, structure, salt content, and organic matter content. Clays have lower water potentials than sands when both have the same water content. Total water potential is the overall effect due to a combination of several potentials, of which matric, pressure, gravity, and solute potentials are the most important. Matric potential (also known as tension or suction potential) represents the interaction of water with soil surfaces and the tendency of small pores to retain water more strongly than large pores. In well-drained soils with low soluble salts, soil water potential is nearly equal to the matric potential. Pressure and gravity water potentials are related to external forces that are exerted on soil water. Pressure potential is due to atmospheric or gas pressure effects, and gravity potential is a result of gravity's pull on soil water. Solute, or osmotic, potential is due to the tendency of water to move from dilute to concentrated solutions.

3.3.1.7 Soil Climate

Discussion of *climate effects* on soils primarily concerns the influence of precipitation and temperature on weathering and degradation rates, and translocation processes. The form (rain and snow) and amount of precipitation determines how much water may enter a soil; however, the topography of an area can cause water to concentrate on portions of the landscape. Also, water may erode the soil surface in which case soil degradation occurs. Weathering and degradation rates are generally faster at higher temperatures, so a combination of increased precipitation and warmer temperatures will enhance soil formation and organic matter decomposition. Snowmelt can also increase the leaching of dissolved inorganic and organic chemicals that have built up in the soil over the course of the winter.

The direction of the slope (*slope aspect*) determines the amount of solar radiation received, which influences soil and air temperatures. In mid-latitudes where the effects of slope aspect are greatest, the slope aspect often determines the type of vegetation growing on south- and north-facing sides of mountains. In the Rocky Mountains, forests can often be observed on north-facing mountain slopes due to cooler temperatures and higher soil moisture levels, whereas rangelands containing sagebrush typically dominate on warmer, drier south-facing slopes.

3.3.2 Soil Physical Processes

Transfer of gases into and out of soils, infiltration and percolation of water, movement of soluble chemical species, and biological activity are controlled to a large degree by soil physical properties. Therefore, processes that maintain healthy soil environments are those that rely on physical characteristics such as porosity or the space not occupied by solids, conditions associated with the amount of water retained or contained in pores, and the ability of particles to migrate via water and wind forces. All the processes discussed below are critical to maintaining a productive environment and soil health.

3.3.2.1 Soil Gas Transfer

As mentioned in the previous chapter, the atmosphere comprises different gases at either relatively constant levels or variable amounts. The soil atmosphere is influenced by the atmosphere because gases flow into and out of soils depending on concentration gradients. As with the atmosphere, primary soil gases are nitrogen (N_2), O_2 , and carbon dioxide (CO_2). Two of the most important soil gases are O_2 and CO_2 , the former critical to plant growth and aerobic microorganisms and the latter a product of respiration. Movement of both of these gases is regulated by both mass flow and diffusion processes; the latter is the most important.

Soil gas concentrations and movement are influenced by soil porosity, soil water contents, biological activity, and the partial pressures of soil gases. When pore spaces are filled with water, gas movement is limited due to the solubility of gas in water and the restriction in gas transfer. As plants and aerobic microorganisms consume O_2 and release CO_2 , gradients are developed that require gas exchange with the atmosphere. Within soils, specific gases move via diffusion as a result of partial pressure gradients that result in higher concentrations of a gas moving toward zones with lower concentrations (see Chapter 10 for a discussion of volatile organic chemical movement in soils). *Macropores* are better conduits for gas transfer, however, as these pores are filled with water or their size reduced due to compaction or filled in with colloids or salts, gas transfer is reduced or completely restricted.

3.3.2.2 Soil Water Movement

Water moves in soils as a vapor or a liquid. *Vapor flow* through a soil is generally a slow process. Water vapor is present in all unsaturated soils and moves by diffusion within the soil due to vapor pressure and temperature gradients. Soil water movement is classified as either saturated or unsaturated flow depending on the soil moisture content (see Figure 2.12). *Saturated flow* occurs in soils where the void space is filled with water. Subsurface horizons can become saturated if water movement is restricted, for example, in soils with a high water table, a clay pan, or in stratified soils. *Unsaturated flow* occurs whenever void spaces are partially filled with air. In both saturated and unsaturated soils, water flow is a function of the driving forces acting on the water (hydraulic gradient) and the ability of the soil to allow water movement (hydraulic conductivity).

Water that infiltrates into soils can be stored, transferred to streams, rivers, lakes, oceans, or become part of the groundwater pool. Surface runoff occurs when rainfall cannot be absorbed by the soil because the rate of infiltration is slow or the soil becomes saturated. Water that falls on land surfaces can be returned to the atmosphere by evapotranspiration, which is a combination of evaporation from soil or plant surfaces and transpiration from plants. Runoff can result in soil erosion and pollution through the transport of soluble and particulate-bound nutrients and pesticides.

3.3.2.3 Soil Erosion

Runoff occurs when precipitation or irrigation water exceeds the infiltration rate of a soil, causing water to run downhill due to gravity, often carrying loose soil material in the overland flow. The greater the angle and the longer the slope, the higher the probability for erosion.

Soil erosion due to water can result in several onsite and offsite problems (Table 3.3). The amount of water that infiltrates or runs off a soil is often determined by the position of the soil in the landscape. Relief, also called *topography*, is the physical landscape characteristic that refers to the angle and length of the slope and proximity of the surface to the water table.

Table 3.3 On-Site and Off-Site Damages Caused by Water Erosion

On-Site	Off-Site
Decrease in organic matter and plant nutrients	Sediment input to water bodies
Loss of topsoil and water-holding capacity	Source of soil and water pollution
Reduction in soil structure	Turbidity of surface waters
Impaired soil biotic communities	Destruction of off-site ecosystems
Reduced crop productivity	Damage to roads and other structures

Predicting soil erosion due to rainfall has been an active area of research for nearly 50 years. Since 1970, modeling efforts have utilized the *Universal Soil Loss Equation* (USLE), and more recently the *Revised Universal Soil Loss Equation* (RUSLE), to evaluate soil loss caused by rainfall and runoff. Both equations are defined by

$$A = R \cdot K \cdot L \cdot S \cdot C \cdot P \quad (3.2)$$

where A is the estimated annual soil loss per unit area that can be averaged over many years; R is the rainfall erosivity factor that depends on intensity, quantity, and duration; K is the soil erodibility factor, which is a function of soil texture, organic matter content, and structure that influence stability and permeability; L and S are topographic factors, length and steepness, respectively; C is the surface-cover factor based on whether a soil is vegetated, mulched, or bare; and P is the management practice factor related to an erosion control application. Although the use of USLE or RUSLE is generally simple, its original development and calibration considered specific conditions that are not truly universal. Improvements in RUSLE have updated, expanded, and enhanced information related to each factor.

In addition to using RUSLE for soil loss estimates, parameters such as the *erodibility index* (EI) can be determined from the following equation:

$$EI = \frac{R \cdot K \cdot L \cdot S}{T} \quad (3.3)$$

which is used in the USDA Conservation Compliance Plan (CCP) to determine if an area warrants federal assistance for erosion control. The value T is an erosion tolerance level that is usually set at 11.2 Mg/ha; however, levels of 2 to 4 Mg/ha have been recommended by some individuals for greater erosion control. An EI value of ≥ 8 indicates the land is highly erodible and in need of special management practices to minimize soil loss, which would also reduce the chance of surface-water contamination by eroded sediments (see Chapter 2).

3.4 SOIL CHEMICAL ATTRIBUTES AND PROCESSES

Mineral solubility, soil reaction (e.g., pH), cation and anion exchange, buffering effects, and nutrient availability are major chemical properties of soils, which are determined primarily by the nature and quantity of the clay minerals and organic matter present. Knowledge of the chemistry of soil solutions is important in understanding how best to handle by-product materials such as animal manures, municipal biosolids, and food by-products. In the following sections we examine clay mineral and organic matter properties, and describe the soil chemical reactions that are controlled to varying degrees by these materials.

3.4.1 Soil Chemical Properties

Clay minerals and organic matter are the primary factors contributing to the chemical reactions in soils; high surface areas and electrical charge characteristics are the reason soils are chemically dynamic. Colloidal mineral and organic particles have extremely high charge-to-area ratios that make them important in processes that include water retention, cation and anion exchange, sorption of inorganic and organic compounds, pH buffering as well as creating numerous other dynamic physical, chemical, and biological soil attributes that are essential to the fertility, structure, and quality of soil environments. In addition, factors associated with acidity, salinity, and sodicity play significant roles in soil chemistry, and have been labeled “master variables” along with a soil’s redox (e.g., oxidation–reduction) status. Soil chemical properties have a profound influence on agricultural production, soil quality and health, and on the overall sustainability of the soil ecosystem.

3.4.1.1 Clay Minerals

Layered aluminosilicate minerals, better known as clay minerals, have a major effect on many soil chemical reactions because of their high “active” surface areas (Figure 3.3). The term *active* refers to charges that develop on clay mineral surfaces and the ability of some types of clay minerals to expand. Clay minerals should not be confused with clay-sized particles because these latter materials can also include particles of quartz, calcite, gypsum, and other minerals that are 2 mm or less in size.

Clay minerals of most interest are crystalline and have regular layers of tetrahedral and octahedral sheets (Figure 3.4). *Tetrahedral sheets* are composed of silicon (Si) and oxygen atoms with three of every four oxygen atoms shared between adjacent tetrahedra. These shared oxygens are referred to as basal oxygens of the tetrahedral sheet; the unshared oxygen is called the apical oxygen. Octahedral sheets are of two types: dioctahedral and trioctahedral. *Dioctahedral sheets* have two of every three octahedral sites occupied, most often by the trivalent aluminum (Al^{3+}) cation. *Trioctahedral sheets* have all octahedral sites occupied with divalent cations, most commonly magnesium (Mg^{2+}).

Layered silicate clay minerals have structures that are 1:1, 2:1, or 2:1:1 layers of tetrahedral and octahedral sheets. The 1:1 clay minerals have one tetrahedral and one octahedral sheet held together by the sharing of the apical tetrahedral oxygen (Figure 3.4). The 2:1 clay minerals have an octahedral

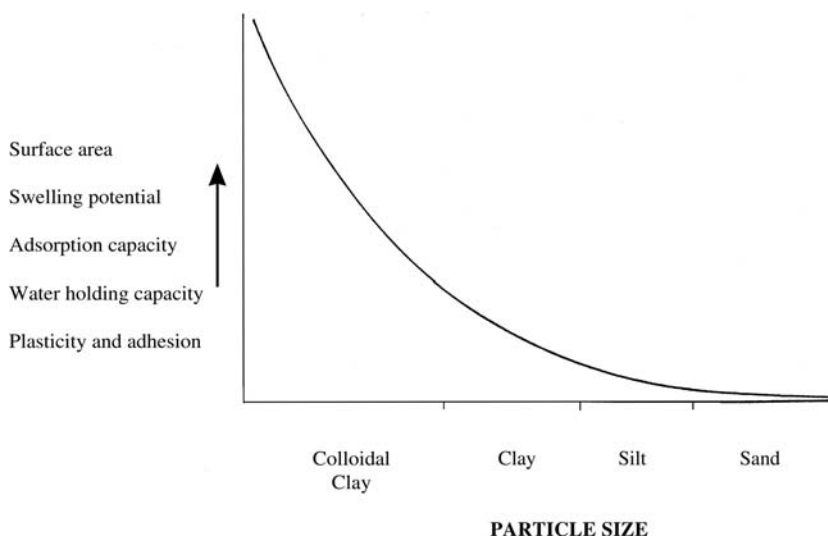


Figure 3.3 Relationship between particle size (using an equivalent weight or volume of material) and several soil chemical and physical properties.

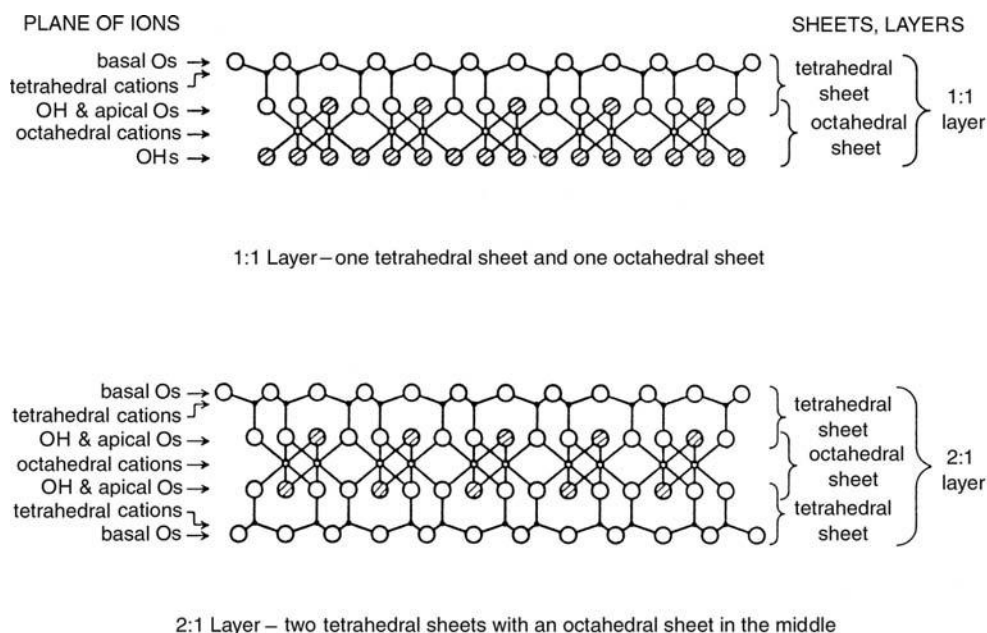


Figure 3.4 Structural representation of 1:1 and 2:1 layers showing the chemical bonds between elements. (Adapted from Schulze, D. G., in *Soil Mineralogy with Environmental Applications*, J. B. Dixon and D. G. Schulze, Eds., Soil Science Society of America, Madison, WI, 2002. With permission.)

sheet sandwiched between two tetrahedral sheets (Figure 3.4). The 2:1:1 layered clay minerals are similar to 2:1 clays with an additional dioctahedral or trioctahedral sheet between 2:1 layers.

Principal clay minerals found in soils are listed in Table 3.4. Kaolinite and halloysite are 1:1 clay minerals that have Si in their tetrahedral sites and Al in octahedral sites. The layers of the 1:1 clay

Table 3.4 Common Clay Minerals Found in Soils throughout the World

Mineral	General Formula ^a
1:1 Layered Minerals	
Kaolinite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$
Halloysite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$
2:1 Layered Minerals	
Illite	$\text{Al}_4(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$
Smectites	
Montmorillonite	$\text{M}_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$
Beidellite	$\text{M}_x\text{Al}_4(\text{Si}_{8-x}\text{Al}_x)\text{O}_{20}(\text{OH})_4$
Nontronite	$\text{M}_x\text{Fe}_4(\text{Si}_{8-x}\text{Al}_x)\text{O}_{20}(\text{OH})_4$
Vermiculite	$\text{Mg}(\text{Al}, \text{Fe}, \text{Mg})_4(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$
2:1:1 Layered Minerals	
Chlorite	$\text{Mg}_6(\text{OH})_{12}(\text{Mg}_5\text{Al})(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH}_4)$

^a M represents a monovalent cation.

minerals are held rather tightly together through *hydrogen bonds* between the basal oxygen of the tetrahedral sheets and the hydroxyls of the adjacent octahedral sheet (see Figure 3.4). Kaolinite is a common 1:1 mineral in soils, particularly in highly weathered soils; halloysite is less stable and is often transformed to kaolinite over time. Illite is a 2:1 nonexpanding, clay mineral that contains nonexchangeable K in the interlayer spaces (i.e., area between the 2:1 layers). Smectites are 2:1 clay minerals that expand and have high surface areas. Montmorillonite is a common smectite found in many soils. Vermiculite is a 2:1 clay mineral that has a high layer charge that holds Mg in its interlayers and is considered nonexpanding when saturated with potassium (K^+) or ammonium (NH_4^+) ions. Chlorite is a common 2:1:1 clay mineral in soil that contains Mg octahedral sheets in its interlayers.

3.4.1.2 Soil Organic Matter

Organic matter plays an important role in the chemistry of soils. Soil properties associated with *soil organic matter* include soil structure, macronutrient and micronutrient supply, cation exchange capacity, and pH buffering. Organic matter is also a source of C and energy for microorganisms. Soil organic matter comprises decomposed plant and animal residues. It is a highly complex mixture of C compounds that also contain nitrogen (N), sulfur (S), and phosphorus (P). Organic matter is made up of humic substances and biochemical compounds. *Humic substances* are operationally defined based on their solubility characteristics: humic acids are soluble in alkaline but not acid solutions, fulvic acids are soluble in acid and alkaline solutions, and humin is the insoluble material that remains after humic and fulvic acid extraction. Biochemical compounds include identifiable organic compounds such as organic acids, proteins, polysaccharides, sugars, and lipids. General properties of soil organic matter and their effect on soils are listed in Table 3.5.

Table 3.5 Soil Organic Matter Properties and Their Associated Effects on Soil

Property	Remarks	Effects on Soil
Color	The typical dark color of many soils is caused by organic matter	May facilitate warming
Water retention	Organic matter can hold up to 20 times its weight in water	Helps prevent drying and shrinking; improves moisture-retaining properties of sandy soils
Combination with clay minerals	Cements soil particles into structural units called aggregates	Permits exchange of gases; stabilizes structure; increases permeability
Chelation	Forms stable complexes with Cu^{2+} , Mn^{2+} , Zn^{2+} , and other polyvalent cations	Enhances availability of micronutrients to higher plants
Solubility in water	Insolubility of organic matter is due to its association with clay; also, salts of divalent and trivalent cations with organic matter are insoluble	Little organic matter is lost by leaching
Buffer action	Exhibits buffering in slightly acid, neutral, and alkaline ranges	Helps to maintain a uniform soil pH
Cation exchange	Total acidities of isolated organic matter fractions range from 300 to 1400 cmol/kg	Increases cation exchange capacity (CEC) of the soil; from 20 to 70% of the CEC of many soils (e.g., Mollisols) is due to organic matter
Mineralization	Decomposition of organic matter yields CO_2 , NH_4^+ , NO_3^- , PO_4^{3-} , and SO_4^{2-}	Source of nutrients for plant growth
Combination with xenobiotics	Affects bioactivity, persistence, and biodegradability of pesticides	Modifies application rates of pesticides for effective control

Source: Stevenson, F. J., *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed., John Wiley & Sons, New York, 1994. With permission.

From an environmental quality standpoint, organic matter can be both beneficial and detrimental. Soil organic matter can sorb *trace element pollutants*, such as lead (Pb), cadmium (Cd), and copper (Cu), which will reduce the chance of contamination of surface waters and groundwaters. Another advantage is the sorption of pesticides and other organic chemicals. This reduces the possibility of pesticide carryover, prevents contamination of the environment, and enhances both biological and nonbiological degradation of certain pesticides and organic chemicals. In addition, soil organic matter is known for its capacity to sorb gases such as nitrogen monoxide (NO), nitrogen dioxide (NO₂), and carbon monoxide (CO).

Although there are many benefits of soil organic matter, there are also *detrimental effects* that occur under certain situations. Soils with high organic matter contents may require higher pesticide application rates for effective control. Water contamination is then a concern if these pesticides are leached or transported by wind or water erosion. Soils also have a finite capacity to sorb trace elements and should not receive extensive applications of organic by-products such as municipal biosolids and animal manures that contain high levels of trace elements. Applications of by-products containing trace elements beyond allowable limits (see Chapter 9) can lead to levels in soils that may be toxic to plants, and possibly to animals and humans upon consumption of foods grown in the contaminated soils or upon ingestion of the soil itself.

3.4.1.3 Soil Acidity

The pH of a soil is an *informative parameter* that provides useful information on what potential controlling factors (e.g., reduced sulfur (S) oxidation, carbonate equilibria, exchangeable sodium (Na⁺)) influence a soil's chemistry. Acid or low pH soils tend to be dominated by Al chemistry and S oxidation–reduction reactions. Soils become acidic by a number of different processes. In humid regions, one of the natural processes associated with weathering that results in the acidification of soils is rainfall exceeding evapotranspiration. *Natural rainfall* is acidic (pH of ~5.6) and continuously adds a weak acid (H₂CO₃) to soils. This acidification results in a gradual leaching of basic cations, e.g., calcium (Ca²⁺), Mg²⁺, and K⁺, from the uppermost soil horizons, leaving Al³⁺ as the dominant exchangeable cation. Exchangeable Al³⁺ is in equilibrium with soluble Al³⁺ in the soil solution that can react with water (e.g., hydrolyze) to produce H⁺ and thus acidify the soil, as shown below and in Figure 3.5:

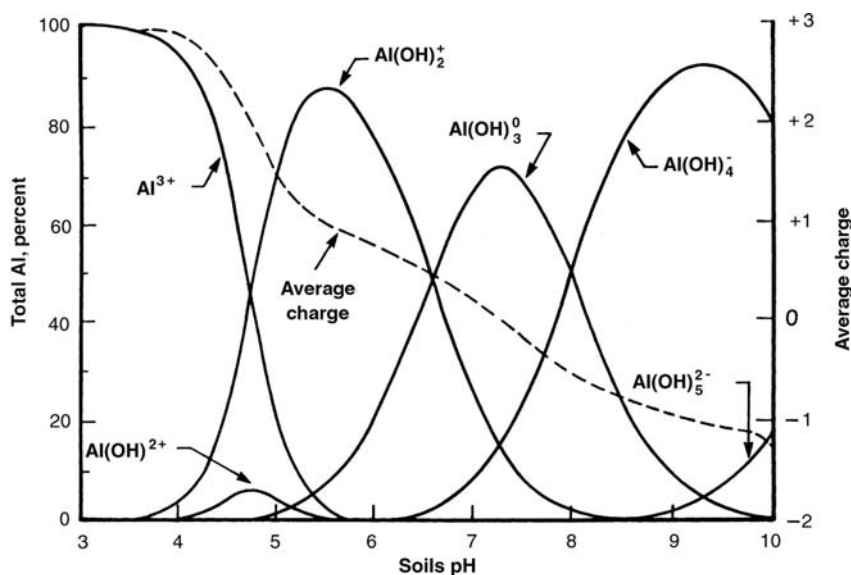
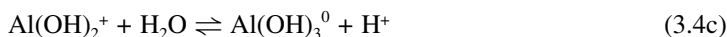
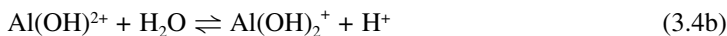


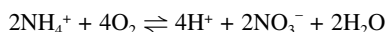
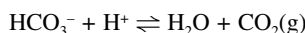
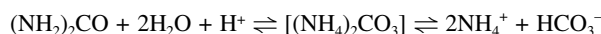
Figure 3.5 Distribution of soluble forms of Al as a function of soil pH. (From Marion, G. M. et al., *Soil Sci.*, 121, 76, 1976. With permission.)



Clays, organic matter, oxides of Al and iron (Fe), and Ca and Mg carbonates (limestones) are the components responsible for pH buffering in most soils and waters. Rainfall containing high levels of acidic substances (see Chapter 11 for more information on acidic deposition) will have a greater impact on sandy, low-organic-matter soils than those higher in clay, organic matter, and carbonates.

Example Problem 3.3

The amount of *liming material* needed to neutralize the acidity from different sources varies based on the H^+ associated with the acid-producing material. For example, if agricultural soils are fertilized with ammoniacal N fertilizers and are not limed properly, they can become acidic over time. Examples include the requirement of approximately 360 kg/ha of lime (as CaCO_3) needed to neutralize the acidity from 100 kg N/ha as urea, $(\text{NH}_2)_2\text{CO}$. The reaction of urea added to soils and its subsequent nitrification is as follows:



which results in the net formation of 2 mol H^+ (e.g., 2 g H^+) for each mole of urea (60 g urea/mol urea or 28 g urea-N/mol urea) and, therefore,

$$100 \text{ kg urea-N/ha} \times 2 \text{ kg H}^+/28 \text{ kg urea-N} = 7.1 \text{ kg H}^+\text{/ha}$$

$$7.1 \text{ kg H}^+\text{/ha} \times 50 \text{ kg CaCO}_3/\text{kg H}^+ = 357 \text{ kg CaCO}_3\text{/ha}$$

Other natural processes that contribute to soil acidification include *plant and microbial respiration* that produces CO_2 and thus H_2CO_3 , mineralization and nitrification of organic N (see Chapter 5), and the oxidation of pyrite (FeS_2) in soils disturbed by mining or drainage (see Chapter 7). Although much of the acidity in soils between pH 4.0 and 7.5 is due to the hydrolysis of Al^{3+} , other contributions include organic acids, exchange reactions, and mineral weathering processes. In extremely acidic soils (pH < 3.0), strong acids such as sulfuric acid (H_2SO_4) are a major component of soil acidity. For most crop production systems, recommended pH values range from 6.0 to 7.0; however, the recommended pH range for organic soils is 5.0 to 6.0.

Excessively acidic soils are undesirable for several reasons. Direct *phytotoxicity* from soluble Al^{3+} or manganese (Mn^{2+}) can seriously injure plant roots, reduce plant growth, and increase plant susceptibility to pathogens. The relationship between Al^{3+} toxicity and soil pH is complicated by the fact that in certain situations organic matter can form complexes with Al^{3+} that reduce its harmful effects on plants. Acid soils are usually less fertile because they lack important basic cations such as K^+ , Ca^{2+} , and Mg^{2+} . Leguminous plants may fix less N_2 under very acidic conditions because of reduced rhizobial activity and greater soil sorption of molybdenum (Mo) (as the MoO_4^-

anion — a key component of *nitrogenase* that is an important enzyme in the N fixation process; see Chapter 5) by clays and Al and Fe oxides. Mineralization of N, P, and S can also be reduced because of the lower metabolic activity of bacteria at low pH levels. It should be noted that many plants and microorganisms adapt to or even prefer very acidic conditions (e.g., pH < 5.0). Examples include ornamentals such as azaleas and rhododendrons and food crops such as cassava, tea, blueberries, and potatoes. In fact, considerable efforts in *plant breeding* and *biotechnology* are directed toward developing Al- and Mn-tolerant plants that can survive in bioregions such as the Tropics where highly acidic soils are commonplace.

3.4.1.4 Salinity and Sodicity

Alkaline soils tend to have high pH levels and contain significant amounts of K, Na, Ca, and Mg salts. Unlike acid soils that are often located in older humid landscapes, alkaline and calcareous (high in free calcium carbonates, CaCO_3) soils tend to develop in younger, less-weathered landscapes. Drier regions such as those characterized as arid or semiarid environments have lower amounts of rainfall to leach salts from the soil profile. This in turn results in a buildup of salts with limited acid cation concentrations. These soils have alkaline pH levels that are greater than 7. If these soils have excessive amounts of salts (i.e., electrical conductivity (EC) > 4 dS/m) they are classified as *saline soils*. However, if they also contain appreciable exchangeable Na (i.e., sodium adsorption ratios (SAR) > 13 or exchangeable sodium percentage (ESP) > 15), they are classified as *saline-sodic*. Finally, if salt concentrations are low (EC < 4 dS/m) and exchangeable Na (SAR > 13 or ESP > 15) high enough to control a soil's physical and chemical attributes, they are classified as *sodic soils*. Recent findings have shown that soil texture and mineralogy will also influence how plant growth will be affected by soils classified under these different conditions.

Salinity and *sodicity* can influence a soil's structure, which in turn affects water infiltration and permeability by reducing water entry into the soil and its hydraulic conductivity. A major reason for the detrimental response to salts and Na is due to swelling of specific clay minerals. Smectite 2:1 clays are more susceptible to the influence of salts and Na, and when swelling occurs there is a reduction in pore size or pores become restricted as slaking occurs. Plant growth is also affected by salinity and sodicity due to the reduction in soil physical properties (e.g., reduced infiltration, permeability, and porosity), nutrient deficiencies, element toxicities and, as the osmotic potential decreases, plant desiccation. Impacts from salinization and sodification can also lead to surface crusts that restrict water and air movement that in turn may promote surface runoff and erosion, limited biological activity, and loss of agronomic production potential and land value.

3.4.1.5 Oxidation–Reduction

Reactions involving the transfer of electrons (e^-) are *oxidation–reduction processes*, and are commonly abbreviated as redox reactions. Oxidation is the loss of electrons, reduction is the gain of electrons, and a soil's redox status is an indication of its water saturation and O_2 content. Redox is controlled by both *abiotic* and *biotic* processes; specific reactions are initiated solely through microbial activity, whereas others occur spontaneously due to chemical means. In aerobic soils, decomposition of organic matter (oxidation) produces electrons that are then accepted by O_2 , forming water (reduction). When O_2 is absent or its rate of diffusion through the soil is limited, as in waterlogged soils or lake sediments, other substances accept the electrons, resulting in the formation of end products other than water (Table 3.6). For example, reactions involving the reduction of nitrate (NO_3^-) (see Chapter 5) in waterlogged environments is a redox process that results in denitrification, which is the conversion of a potential aquatic pollutant (NO_3^- -N) to gaseous

Table 3.6 Redox Reactions of Primary Importance in Waterlogged Soils; Elements or Compounds Involved in Redox Reactions

Element	Oxidized Species	Reduced Species	Redox Potential for Reaction (mV) ^a
O	O ₂ [$\frac{1}{2}\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{O}$]	H ₂ O	700 to 400
N	NO ₃ ⁻ [$\text{NO}_3^- + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{NO}_2^- + \text{H}_2\text{O}$]	NH ₄ ⁺ , N ₂ O, N ₂	220
Mn	Mn ⁴⁺ (manganic: MnO ₂) [$\text{MnO}_2 + 2\text{e}^- + 4\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$]	Mn ²⁺ (manganous: MnS)	200
Fe	Fe ³⁺ (ferric: Fe(OH) ₃) [$\text{FeOOH} + \text{e}^- + 3\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + 2\text{H}_2\text{O}$]	Fe ²⁺ (ferrous: FeS, Fe(OH) ₂)	120
S	SO ₄ ²⁻ (sulfate) [$\text{SO}_4^{2-} + 8\text{H}^+ + 7\text{e}^- \rightleftharpoons \frac{1}{2}\text{S}_2^{2-} + 4\text{H}_2\text{O}$]	S ²⁻ (sulfide: H ₂ S, FeS)	-75 to -150
C	CO ₂ (carbon dioxide) [$\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$]	CH ₄ (methane)	-250 to -350

^aRedox potentials are approximate values and will vary with soil pH and temperature.

N oxides and N₂. An example of an important abiotic oxidation reaction is the transformation of reduced S minerals such as pyrite, FeS₂, in acid mine drainage (Essington, 2004), which is described in more detail in Chapter 7.

The *sequence of reduction* in waterlogged environments is well understood; hence, a knowledge of the redox potential of a system can be used to predict the dominant electron acceptors present. Information presented in Figure 3.6 illustrates the redox transformations that occur when a soil is saturated with water. (Note that trends in this figure will vary with pH and temperature; Figure 3.6 assumes a pH of 7.0.) Available O₂ is depleted within 1 day; NO₃-N becomes the next substrate for electrons produced by anaerobic decomposition of organic matter, followed by Mn oxides and then Fe oxides. As the *redox potential* (Eh) declines, easily reducible solid forms of Mn disappear and exchangeable Mn²⁺ accumulates, followed by Fe²⁺ as Fe oxides are reduced. Only when all sources of NO₃-N, Mn⁴⁺, and Fe³⁺ have been depleted will the reduction of SO₄²⁻ to sulfide (S²⁻) occur, followed by the anaerobic degradation of organic C that results in the production of methane (CH₄), often referred to as “swamp or marsh gas.” Should a soil such as this dry out and aerobic conditions be reestablished, the reactions will often reverse; NO₃-N will begin to accumulate as organic matter is mineralized and the soluble Mn and Fe will begin to form insoluble precipitates such as MnO₂ and Fe(OH)₃. For an element such as P, where sorption by Fe oxides is an important mechanism of retention in soils, alternating wet and dry cycles can affect both plant uptake and the potential for delivery of P to nearby aquatic systems that are sensitive to eutrophication (see Chapter 6). Research has shown that the development of anaerobic conditions in lake sediments can reduce Fe oxides and Fe phosphates, resulting in a release of soluble P from these solid phases, increasing the likelihood of *eutrophication*. Attempts to construct wetlands or riparian zones near agricultural fields to enhance denitrification should, therefore, consider the possibility that this could increase the release of soluble P into streams and rivers bordering these fields.

Other transformations that occur in *waterlogged environments*, such as the fate of organic compounds (e.g., pesticides, hydrocarbons in storm-water runoff) or trace elements, have received less study; hence they are not as well understood as those involving plant nutrients. This will be particularly important should the use of constructed wetlands as biological filtration zones for urban and industrial wastes increase in the future.

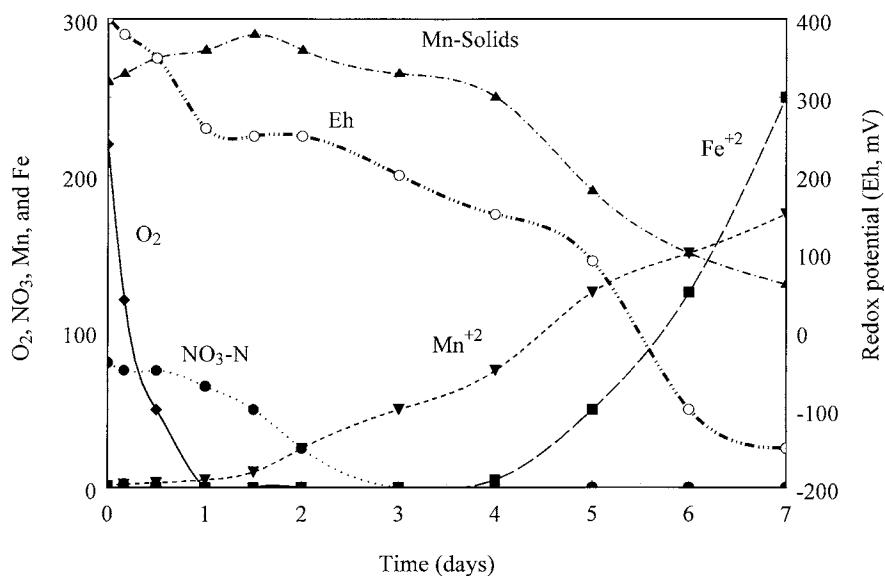


Figure 3.6 Schematic representation of the transformations than can occur when a soil (pH = 7.0) is saturated with water and anoxic conditions develop. (Based on data from Turner and Patrick, 1968.)

3.4.2 Soil Chemical Processes

Abiotic chemical reactions and transformations determine to a large degree how soil ecosystems evolve, how introduced substances are either positively or negatively affected (i.e., retained, altered, or removed), and how both soil physical and biological components are influenced. Soil chemical processes range from rapid reactions involving sorption and/or kinetic responses to added substances to geologically slow processes that transform rocks to soils via formation of secondary minerals. Soil formation is a result of several physical, chemical, and biological processes, but at any one time, the chemical process that most often influences the fate and mobility of a contaminant is that of sorption.

3.4.2.1 Mineral Weathering

Change in soil mineral composition is a slow process that involves physical and chemical weathering, loss of soluble constituents, and *in situ* formation of *secondary minerals*. Easily weathered minerals will be altered initially followed by more resistant minerals. Clay minerals play an important role in soil chemistry, health, and function. Therefore, modification of parent materials to secondary aluminosilicates must be appreciated to understand how clay minerals influence soils. For example, Figure 3.7 describes the general conditions that influence the formation of clay minerals and oxides. Some *primary aluminosilicate minerals* are physically and chemically weathered to produce clay minerals. Muscovite altered to illite is a good example of this. Both muscovite and illite have 2:1 structures; however, the combination of physical breakdown, loss of K ($-K$), and a slight alteration in the muscovite structure produces illite, which has a lower cation exchange capacity and greater swelling potential. Some clay minerals are recrystallized products of ions released during the breakdown of other minerals. Formation of kaolinite, a 1:1 clay mineral, is the result of recrystallization because there are no primary or secondary minerals with analogous 1:1 structures. As noted in Figure 3.7, kaolinite forms directly from the ions released from the weathering of primary aluminosilicates or smectite if accompanied by a rapid loss of basic cations. Intense weathering is responsible for the loss of silica (Si) and the production of Fe and Al oxides.

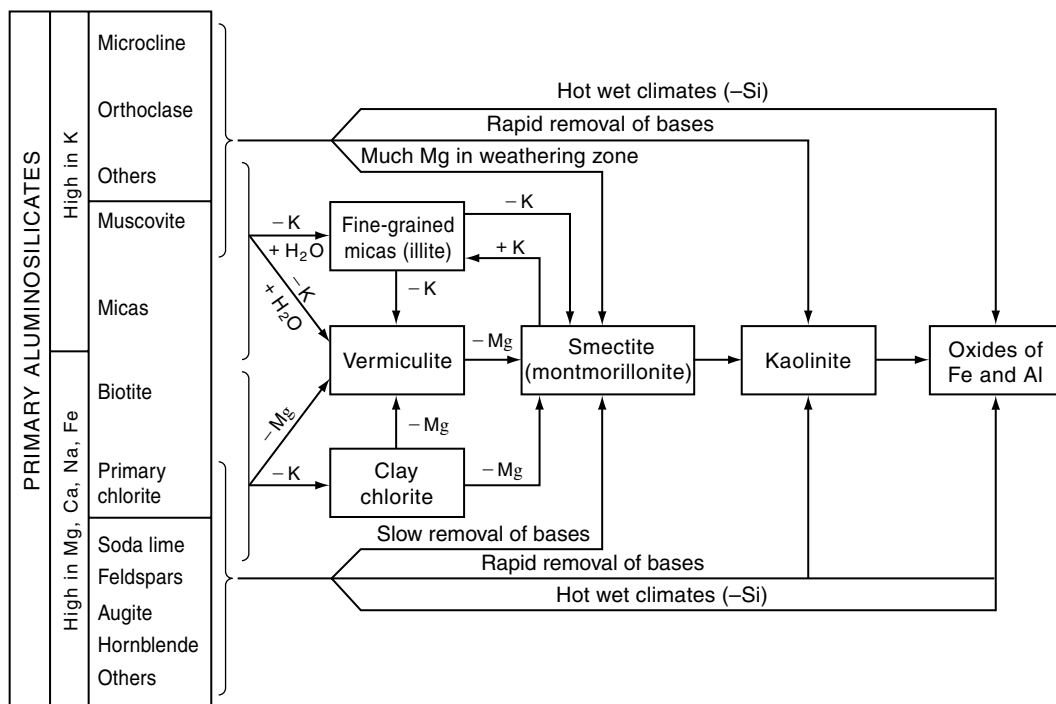


Figure 3.7 Sequence for the formation of clay minerals and Fe and Al oxides. Note the loss of soluble cations in the genesis of clay minerals. (From Brady, N. C. and R. R. Weil, *Elements of the Nature and Properties of Soils*, 2nd ed., Prentice Hall, Upper Saddle River, NJ, 2004. With permission.)

3.4.2.2 Cation and Anion Exchange

Ion exchange is one of the most significant functions that occur in soils. Ion exchange is a consequence of mineral charge that is derived from isomorphous substitution, broken edges, and pH-dependent charge sites. For organic matter, most of the charge is related to the pH-dependent characteristics of organic acid functional groups. Charged sites can also develop as a function of pH with different clay minerals, metal oxides, and organic matter. These charged sites are the result of ionization (H^+ dissociation) or protonation of uncharged sites; ionization results in a negative-charged site and protonation a positive-charged site. Both of these reactions are dependent on pH and are called pH-dependent charge. As the pH increases, the cation exchange capacity of the soil is generally greater due to an increase in the number of pH-dependent charged sites. Under acid soil conditions, some clay minerals, metal oxides, and organic matter will have positively charged, anion exchange sites. Inorganic and organic ions having charges that are opposite of the exchange site are attracted or sorbed to the soil surface by electrostatic processes.

Isomorphous substitution occurs when an element substitutes for another in the mineral structure, such as Al^{3+} substituting for Si^{4+} . If an element of a lower charge substitutes for an element of a higher charge, a permanent negative charge develops in the clay mineral. Both kaolinite and halloysite are 1:1 clays that have very little surface charge due to low isomorphous substitution in their structures. Illite, or hydrous mica, is a 2:1 nonexpanding, dioctahedral clay mineral, which has K in the interlayer spaces (i.e., area between the 2:1 layers). The K atom is held tightly in the interlayers and is commonly referred to as being nonexchangeable. Montmorillonite is one of several types of clay minerals in the smectite family. Smectites are 2:1 clay minerals that have low to moderate isomorphous substitution. Because of the low permanent charge, smectites are capable of expanding, thus increasing the amount of exposed surface area. The high surface area together with the number of charged sites give smectites the ability to adsorb cations. *Cation exchange*

capacity is the amount of exchange sites that can adsorb and release cations. Montmorillonite is a common smectite in most soils. Vermiculite is a 2:1 clay mineral that has high isomorphic substitution. The interlayers of vermiculite contain exchangeable Mg^{2+} ions. However, because vermiculite has a higher layer charge, interlayer Mg^{2+} in vermiculite is held more tightly than is interlayer Mg^{2+} in smectite. Although vermiculite has a high cation exchange capacity, when saturated extensively with K^+ or NH_4^+ ions, vermiculite becomes nonexpanding. Chlorite is also prevalent in many soils. The interlayer space between the 2:1 layers in chlorite is occupied by Mg octahedral sheets, thus making this a 2:1:1 layered silicate. Chlorites have low surface area due to the attraction of the brucite layer (Mg octahedral sheet) by the 2:1 layers, which reduces their potential cation exchange capacity.

Both clay minerals and organic matter have the ability to sorb soluble substances from the soil solution. This is an important means by which plant nutrients are retained in crop rooting zones. On the other hand, facilitated transport is a process involving the sorption of dissolved chemical species by *colloidal-size particles* (e.g., clays and dissolved organic matter) that can leach through soils and transport heavy metals, organic chemicals (e.g., pesticides), and other potential pollutants.

3.4.2.3 Sorption

Sorption is the general term used to describe several chemical processes (e.g., adsorption, partitioning, surface precipitation, polymerization, and formation of secondary solid phases) that result in a substance (sorbate) being retained by soil inorganic and organic solid phases (sorberent). Sorption is often the preferred term when the mechanism of retention of a sorbate is unknown as is often the case with P and many organic chemicals. Sorption is defined as the net accumulation of a sorbate at an interface between a sorberent and the solution phase. Sorption can occur due to physical processes involving van der Waals forces or electrostatic outer sphere complexes, for example, anion exchange, which is referred to as nonspecific adsorption, to chemical processes such as inner-sphere complexes, ligand exchange, and chemisorption, many of which are referred to as specific adsorption.

Major factors influencing sorption processes are well known and include clay type and content, oxides and hydroxides of Al and Fe, carbonates, and soil organic matter. In addition, the effects of soil solution chemistry (e.g., pH, ionic strength, competing ions, and redox) and climatic conditions that affect soil temperature and moisture also influence sorption processes. Sorption can vary with soil depth and is affected by cultural operations such as fertilization, liming, manuring, or reduced tillage practices that can alter soil physical, chemical, and biological properties. Sorption of most substances is a function of pH that influences the sorbate and sorberent structure or composition. For example, anion (e.g., H_2PO_4^- , SeO_3^{2-} , F^-) sorption is usually greater at low pH levels due to greater protonation (e.g., $>\text{O}^- \rightarrow >\text{OH} \rightarrow >\text{OH}_2^+$) and formation of positively charged surfaces formed on clays and metal oxides with decreasing soil pH; the opposite is generally true for cations.

Sorption can be quantified by using mathematical equations that relate the amount of sorbate retained by the sorberent (x/m) to the concentration in solution at equilibrium (C_e). The four basic types of *sorption isotherms* are shown in Figure 3.8. The *L*-curve isotherm represents a sorbate that has a high affinity for the sorberent at low concentration, but at high concentrations the affinity (and number of sorption sites) decreases. When a sorbate has a very high affinity for the sorberent, the type of isotherm is characteristic of an *H*-curve. The *S*-curve suggests there is a barrier to sorbate sorption at low concentrations, which may be due to other substances competing for sorption sites, but once this limitation is overcome, the sorbate–sorberent interaction is similar to the sorption indicative of the *L*-curve. The last isotherm type, the *C*-curve, is characteristic of constant sorption that suggests sorbate retention is independent of surface coverage. As described below, *C*-curve sorption processes often involve organic chemicals partitioning by soil organic matter.

Sorption data are usually obtained by reacting soils or sediments with solutions ranging in initial sorbate concentrations over a certain time period. Two commonly used approaches to quantifying

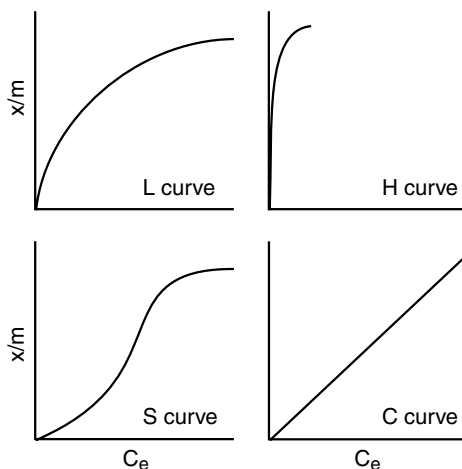


Figure 3.8 Various types of isotherms that result from sorption of inorganic and organic sorbates by different environmental sorbents.

the soil sorption process are the *Freundlich* and *Langmuir* mathematical models; another recently proposed model is called the *initial mass* (IM) isotherm.

The *Freundlich sorption equation* is

$$x/m = K_f C_e^{1/n} \quad (3.5)$$

where

x/m = mass of sorbate sorbed per unit weight of sorbent

K_f and $1/n$ = empirical constants

C_e = equilibrium concentration of the organic chemical

The value of K_f is a measure of the extent of sorption. The linear form of the Freundlich equation is obtained by logarithmic transformation:

$$\log(x/m) = \log K_f + 1/n \log C_e \quad (3.6)$$

A plot of $\log(x/m)$ (y-axis) vs. $\log C_e$ (x-axis) should produce a straight line, with $1/n$ equal to the slope and $\log K_f$ the intercept.

The *Langmuir sorption equation* is

$$x/m = K_1 C_e b / (1 + K_1 C_e) \quad (3.7)$$

where

x/m and C_e = the same as described above

K_1 = sorption constant related to binding strength

b = maximum amount of sorbate sorbed by the sorbent

One of the linear forms of the Langmuir equation that can be used to determine K_1 and b is

$$C_e / (x/m) = 1/K_1 b + C_e / b \quad (3.8)$$

If a plot of $C_e/(x/m)$ vs. C_e is a straight line, then the sorption data conform to the Langmuir equation, and b can be calculated from the slope ($1/b$) and K_1 from the intercept ($1/K_1b$).

Although Freundlich and Langmuir equations do not provide mechanistic information about the sorption process or kinetic reactions, they are useful in comparing sorption capacities among soils or changes in sorbate sorption due to varying soil conditions (e.g., pH, ionic strength, organic matter) or variations in long-term management practices (e.g., manuring, tillage, cropping). These equations are also used to approximate the quantity of nutrients such as P that must be sorbed by various soils to raise the P concentration in the soil solution at equilibrium to a desired, or maximum value.

The IM isotherm has been shown to fit sorption of several sorbates (F^- , PO_4^{3-} , SO_4^{2-} , NO_3^- , dissolved organic carbon (DOC)) by a forest soil better than Langmuir and Freundlich models (Nodvin et al., 1986), which were unable to provide a linear relationship or be transformed for use in the linearization process (Figure 3.9). The *IM isotherm* is written in the form of

$$x/m \text{ (adsorbed or released)} = mC_i - b \quad (3.9)$$

where

x/m = as defined above

m = slope

C_i = initial amount of sorbate added with respect to the sorbent

b = intercept

If a plot of x/m vs. C_i is linear, both m (slope) and b (y -intercept) can be determined. Because native sorbate levels are high in some soils, there are cases where sorbate release occurs (i.e., when b is negative), particularly for NO_3^- . The sorbate *reserve soil pool* (RSP) can be calculated from the IM isotherm as

$$RSP = -b/(1 - m) \quad (3.10)$$

The RSP is a measure of the labile sorbate, and is an estimate of the potential level of biologically active sorbate in a soil.

Sorption of hydrophobic organic chemicals (HOC) by soil organic matter is quantified by using the linear sorption equation to determine *distribution coefficients*,

$$x/m = K_d C_e \quad (3.11)$$

where x/m and C_e are as defined above, and K_d is the distribution coefficient that is related to the amount of sorbate sorbed per sorbent. Because a sorbate's K_d value increases with increasing soil organic matter, another relationship that is commonly used that expresses sorption as a function of the amount or fraction (f) of soil organic carbon (OC) is the *organic carbon–water partition coefficient*, K_{OC} .

$$K_{OC} = K_d/f_{OC} \quad (3.12)$$

For a specific HOC, the larger the K_{OC} , the greater is its partitioning into the soil organic phase. When K_{OC} are known for specific HOC, the distribution coefficient can be calculated for any soil with a known OC content.

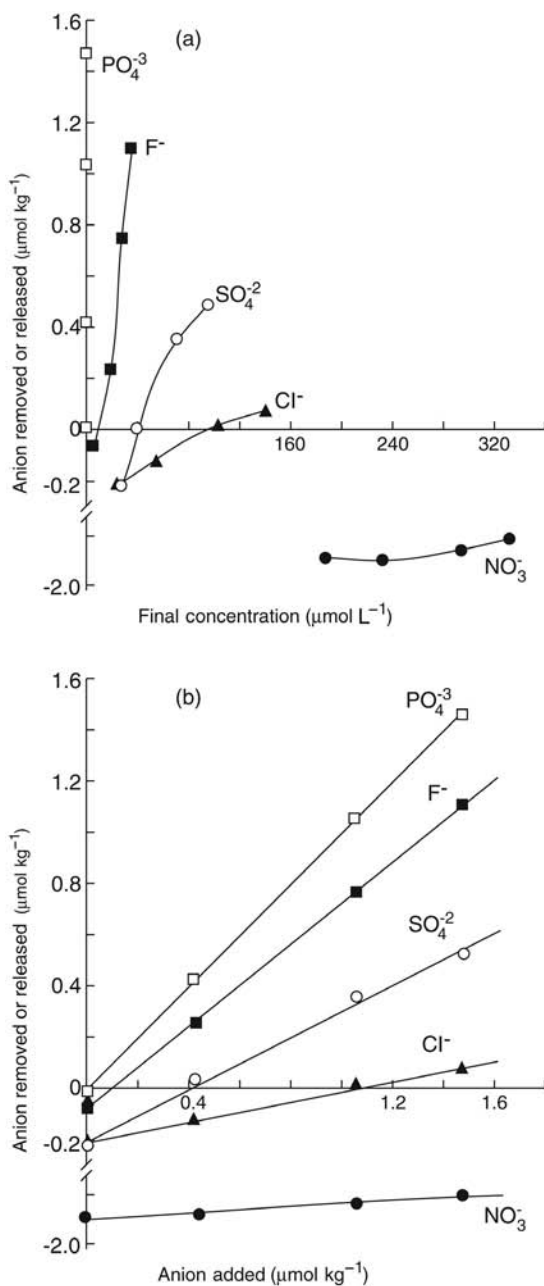


Figure 3.9 Examples of sorption studies evaluating PO_4^{3-} , F^- , SO_4^{2-} , Cl^- , and NO_3^- retention by a sandy loam forest soil using (a) final solute concentration and (b) initial mass of anions added. Positive ordinate (y-axis) values indicate anion adsorption, whereas negative values represent anion release. (Modified from Nodvin, S. C. et al., *Soil Sci.*, 142, 27, 1986.)

Example Problem 3.4

Sorption of Cd was studied using 2 g soil samples placed in six test tubes that contained 40-mL solutions of different initial Cd concentrations. After shaking for an equilibration time of 24 h, the solutions were separated and the supernatant analyzed for Cd. From the data below, determine the type of adsorption curve and the best fit for Freundlich, Langmuir, and IM isotherms represented by Cd sorption.

Initial Cd Concentration (mg/L)	Final Cd Concentration (C_e) (mg/L)
1	0.12
2	0.14
4	0.19
8	0.26
16	0.42
32	0.75

A graph of the amount of Cd sorbed per mass of soil (mg Cd/kg soil) vs. the equilibrium Cd concentration (C_e) indicates the sorption of Cd follows the *H*-curve, which suggest Cd has a high affinity for the soil. Freundlich, Langmuir, and IM sorption isotherms result in the following linear equations:

$$\begin{array}{lll} \text{Freundlich} & y = 1.87x + 3.15 & r^2 = 0.96 \\ \text{Langmuir} & y = -0.06x + 0.005 & r^2 = 0.44 \\ \text{Initial Mass} & y = 0.98x - 2.02 & r^2 = 0.98 \end{array}$$

Based on these results, Cd is strongly sorbed by the soil and conforms to both Freundlich and IM sorption isotherms.

3.5 SOIL BIOLOGICAL ATTRIBUTES AND PROCESSES

The part of the planet that supports life is described as the *biosphere*. Thus, the biosphere comprises all living organisms and their general surroundings, and includes most hydrosphere and soil ecosystems. Living organisms that are considered essential to biosphere communities include aquatic and terrestrial plants, animals, and microorganisms. Ecosystems that comprise different parts of the biosphere are geographic entities defined by natural features. Although we typically confine ourselves to regions that have political boundaries, such as cities, states, and countries, environmental quality and protection should be a concern to all of us. Biosphere impacts, both positive and negative, are often the result of lifestyles that rely on natural resources.

Plants, animals, and microorganisms play a significant role in the formation of soils and their physical, chemical, and biological characteristics. Plants cycle nutrients taken from the atmosphere and soil, converting them to plant tissue, which, after dying, is decomposed by soil microorganisms and recycled back to the soil. Soil organic matter is derived from both plant decomposition and synthesis reactions by soil microorganisms and is important in processes involving weathering, degradation, and translocation of nutrients as well as contaminants. Some soil organic compounds can influence pH and movement of dissolved ions to lower depths. *Respiration* of CO_2 by plant roots and microorganisms can also increase acidity, e.g., H_2CO_3 formation, resulting in lower soil pH, which occurs predominantly in areas where intense respiration occurs. Physical mixing of soil particles and organic matter by soil animals can either enhance or decrease soil formation.

3.5.1 Soil Biological Constituents

Biological communities vary from soil to soil and range from plant roots, rodents, worms, and insects, all of which are usually visible to the eye, to microorganisms (bacteria, actinomycetes, fungi, algae, and protozoa) that are often so small a microscope is required to see them. The relative number and total biomass (weight of organism per unit volume) are given in Table 3.7 for a surface soil (note the extremely large number of microorganisms).

Organisms inhabiting soil environments can be grouped into two broad categories. These categories include the *autotrophs*, which assimilate C from CO_2 and obtain energy from sunlight or through the oxidation of inorganic compounds, and the *heterotrophs*, which use organic C as a source of energy and C. The autotrophs are considered producers because of their ability to convert

Table 3.7 Estimated Number and Biomass of Soil Animals and Microorganisms in Surface Horizons to 15 cm; Deeper Depths Used for Earthworms

Organisms	Abundance		Biomass (kg/HFS)
	Per Meter ²	Per Gram	
Soil Animals			
Protozoa	10 ⁹ –10 ¹⁰	10 ⁴ –10 ⁵	20–200
Nematodes	10 ⁶ –10 ⁷	10–10 ²	10–150
Mites	10 ³ –10 ⁶	1–10	5–150
Earthworms	10–10 ³	<1	110–1,500
Others	10 ² –10 ⁴	Variable	10–100
Microorganisms			
Bacteria	10 ¹³ –10 ¹⁴	10 ⁸ –10 ⁹	400–5,000
Actinomycetes	10 ¹² –10 ¹³	10 ⁷ –10 ⁸	400–5,000
Fungi	10 ¹⁰ –10 ¹¹	10 ⁵ –10 ⁶	1,000–15,000
Algae	10 ⁹ –10 ¹⁰	10 ⁴ –10 ⁵	10–500

Note: Biomass values based on live weight per hectare furrow slice (HFS) to a depth of 15 cm, with dry weights approximately 25% of these values.

Source: Brady, N. C. and R. R. Weil. *Elements of the Nature and Properties of Soil*, 2nd ed., Prentice Hall, Upper Saddle River, NJ, 2004. With permission.

CO₂ and energy from the sun into organic C products, a process called *photosynthesis*. Only vascular plants and some bacteria and algae are considered producers. Heterotrophs, on the other hand, are regarded as consumers and decomposers. Soil animals and most microorganisms fall into this category.

3.5.1.1 Plants

Aboveground plant parts are a source of food for consumers such as grazing animals and humans. Belowground plant parts (i.e., roots, tubers, and other organs) are a source of food for humans and animals as well as soil consumers and decomposers, and influence the type and activity of microorganisms living in and around the plant roots. The *rhizosphere* is the area around roots that is influenced by the presence of the roots; it often has from 10 to 100 times more microorganisms than the bulk soil. Root exudates include organic and inorganic substances that provide nutrients for the rhizosphere microorganisms.

Symbiotic associations between plant roots and microorganisms result in a variety of beneficial effects to both the plant and the microbes. Nodules that form on leguminous plant roots are caused by bacteria that are capable of converting atmospheric N₂ into N compounds utilizable by the plant (see Chapter 5, Section 5.2.4). Mycorrhizal fungi form symbiotic relationships with plant roots. Plants benefit from this association by increased absorption of nutrients (e.g., N, P, S, and micronutrients) and water.

3.5.1.2 Soil Animals

Soil animals include all subterranean animals that in one way or another influence soil properties. Large animals such as cattle and deer can also influence soils primarily through overgrazing, which influences the vegetative community structure, function, and health. Effects of overgrazing include reduced ground cover, altered plant species composition, soil compaction, and possibly soil erosion. Small burrowing animals can have a great impact on soil properties.

Gophers, shrews, prairie dogs, badgers, moles, ground squirrels, and mice are some of the burrowing animals that can profoundly influence the development of soils by mixing topsoil and subsoil materials. Tunnels and holes produced by burrowing animals will increase the infiltration of water and air. Subterranean soil animals include arthropods (e.g., ants, beetles, centipedes, millipedes, mites, spiders, springtails), worms (e.g., nematodes, earthworms), and protozoa. Protozoa and nematodes are generally the most abundant of all soil animals (Table 3.7 and Figure 3.10); protozoa are, in a strict sense, classified as microorganisms and are therefore discussed in the next section.

Several *arthropods* are involved in the decomposition of plant materials and also assist in mixing the fragmented vegetative parts into the soil. Ants are capable of bringing coarse-textured material up from below the soil surface to build their mounds. Worms are excellent soil-forming animals known for their ability to enhance soil fertility and physical properties. Millipedes are primarily saprophytic and consume dead organic materials, whereas ants and termites, as well as prairie dogs, can mix large volumes of soil through their tunneling efforts.

Earthworms play an important role in soil formation and breakdown of organic residues. They are usually found in the organic-rich surface horizon, but some species burrow as deeply as 6 m. Earthworms ingest organic residue and soil, which are then decomposed by digestive enzymes and grinding action as they pass through the worm's gut. Each day, the weight of soil material ingested and excreted by earthworms can be equivalent to their body weight. The amount of earthworm casts (excreted material) produced yearly in a hectare of land has been estimated to range from 70

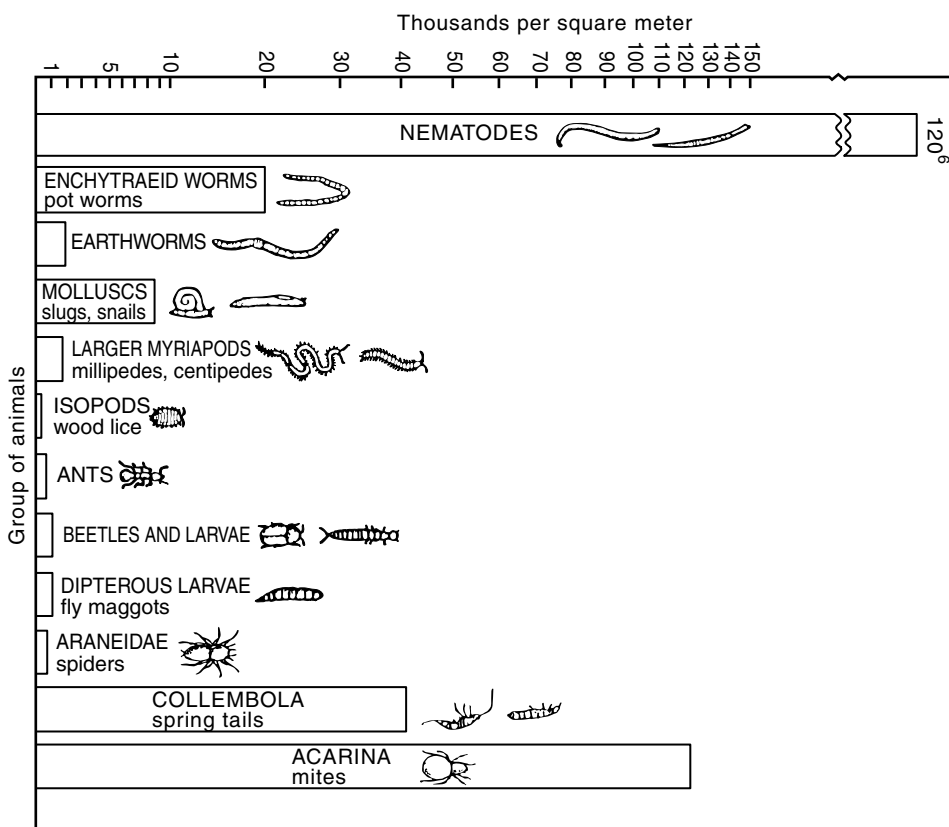


Figure 3.10 Illustration of the types of soil animals and their numbers determined in a square meter of a grassland soil. (From Paul, E. A. and F. E. Clark, *Soil Microbiology and Biochemistry*, Academic Press, San Diego, CA, 1989. With permission.)

to 250 Mg/ha. These casts have been shown to increase the availability of the nutrient elements N, P, K, Ca, and Mg compared with original soil material. *Lumbricus terrestris*, the common earthworm, is one of more than 1800 worm species known worldwide.

Nematodes are microscopic, unsegmented roundworms that are classified based on their feeding habits. The most common are those that feed on decaying organic matter; however, others prey on bacteria, fungi, algae, or other nematodes, or they infect plant roots. One method of controlling the latter type of nematodes is by soil fumigation, although this method of control can be very costly and potentially harmful to the environment if not managed carefully. Crop rotation has been shown to be a very effective practice for controlling not only pests such as the nematodes, but also insect and disease problems and is also beneficial to soil fertility. Innovative efforts have been used to control the sugar beet nematode (*Heterodera schachtii*) by including trap crops, usually radish species, that act as surrogate crops that are colonized by the nematode, and are also able to impair normal nematode reproduction.

3.5.1.3 Soil Microorganisms

Soil microorganisms include *bacteria*, *actinomycetes*, *fungi*, *algae*, and *protozoa*. *Viruses*, which only grow in other living cells, are molecules of RNA or DNA within protein coats and are discussed here because they play an important part in the microbiology of soils. Viruses require a viable metabolizing host organism in order to reproduce or duplicate. They induce the host organism to manufacture the necessary components for virus reproduction. Many viruses can cause diseases such as those found in plants (e.g., tobacco mosaic and potato leaf roll) and animals (e.g., foot-and-mouth disease and bovine leukemia). Survival of viruses that are pathogenic to humans and animals, and which are known to be in municipal wastewaters and biosolids, animal manures, and lagoons, as well as household septic wastes, is a potential concern when these materials are used in a land application program.

Bacteria are the most numerous of all soil microorganisms (Table 3.7), and individual bacterial cells are the smallest and most difficult to see under the microscope. A handful of soil can contain several billion bacterial cells. The ability of bacteria to reproduce rapidly and adapt to new environmental situations is important to the decomposition and transformation of both natural and anthropogenic products. Some of the functions performed either entirely or in part by bacteria include nutrient cycling, decomposition of organic materials, N fixation, pesticide detoxification, and oxidation–reduction reactions. Without bacteria to mediate these processes, life as we know it would not be possible.

Bacteria are classified as either *autotrophs* or *heterotrophs*, depending on their sources of energy and C. They can be further grouped as aerobes (require O₂), anaerobes (do not require O₂), and facultative anaerobes (grow in the presence or absence of O₂). The type and abundance of any one group of bacteria depend on such factors as available nutrients and soil environmental conditions. Some of the aerobic and anaerobic bacteria form spores that allow them to survive under adverse environmental conditions during dry and high temperature periods. Soil conditions that affect the growth of bacteria are many; however, the most important factors are the O₂, temperature, moisture, acidity, and inorganic and organic nutrient status of the soil. Bacteria and fungi are usually active in aerated soils, but in ecosystems containing little or no O₂, most of the biological and chemical transformations are governed by bacteria. Optimum temperature and moisture requirements for most bacteria are 20 to 40°C and 50 to 75% of the moisture-holding capacity of the soil, although specialized groups are active at higher and lower temperatures and moisture contents. Extremely high and low pH are generally not suitable for most bacteria, but there are specialized bacteria that are active in soils with pH levels less than 3 and others above pH 10.

Actinomycetes physiologically resemble bacteria; however, their slender branched filaments also resemble filamentous fungi. In most soils, bacteria and fungi are more numerous than actinomycetes (Table 3.7), but in some warm climate soils, actinomycete biomass may exceed that of

others. Although actinomycetes may not be as important as bacteria and fungi for carrying out biochemical processes, they are known to be involved in the decomposition of some resistant components of plant and animal tissues (e.g., cellulose, chitin, and phospholipids), synthesis of humic-like substances from the conversion of plant remains and leaf litter (i.e., green manures, compost piles, and animal manures), infection of plants, animals, and humans, and excretion of antibiotics or production of enzymes that can influence soil community composition. The “earthy” aroma of soils is largely caused by a volatile compound produced by actinomycetes.

Fungi obtain their energy and C from the decomposition of plant and animal remains, or soil organic matter. Two groups of fungi common to soils are the unicellular organisms called yeasts and the multicellular filamentous organisms, such as molds, mildews, smuts, and rusts, which are the most prevalent. Filamentous fungi are abundant in well-aerated fertile soils, whereas yeast inhabit anaerobic environments. The filamentous bodies, which individually are called hyphae and collectively mycelia, are found interwoven among soil particles, organic matter, and plant roots. Mushrooms are the true reproductive structures of a filamentous fungi that may have extensive hyphae below the ground. Fungi also perform several functions in soil, including decomposing plant and animal organic substances, binding of soil particles into aggregates, forming symbiotic (mycorrhizal) associations with plants, and acting as a predator in controlling certain microorganisms and soil animals. In acid surface layers and forest soils, fungi make up the majority of the soil biomass and are most active in organic matter decomposition.

Algae, like vascular plants and some bacteria, are capable of performing photosynthesis because they contain chlorophyll. In soil with moist and fertile conditions, algae can potentially produce several hundred kilograms of organic substances per hectare on an annual basis. Blue-green algae are capable of fixing atmospheric N_2 into organic N compounds. Lichens, which are a symbiotic association of an algae and a fungus, are commonly the first colonizers of bare rock and soil parent material. Organic acids synthesized and released by lichens are known to weather rock surfaces, which plays an important role in the early stages of soil development in some areas.

Protozoa are unicellular animals that are primarily microscopic in size. Some protozoa, however, are known to reach macroscopic dimensions. They feed on decomposing organic matter and organisms such as bacteria and sometimes other protozoa. Protozoa populations are often related to bacteria numbers; as bacteria increase following the addition of organic residues to soils, protozoa increase as well.

3.5.2 Soil Biological Processes

In addition to both physical and chemical influences on contaminant fate and transfer, biological processes must be considered in how environments are modified (e.g., pH and redox reactions), inorganic substances are transformed, and organic chemicals are degraded. Particular emphasis is placed on the role microorganisms play in the biodegradation and transformation of contaminant substances. Several important factors control biological population dynamics and overall activities of organisms that render both inorganic and organic contaminants harmless.

3.5.2.1 Factors Influencing Soil Organisms

Factors such as rainfall, temperature, vegetation, and physical and chemical properties of soils influence the type and number of living organisms in a soil community. Optimal moisture and temperature are important for microbial proliferation; however, lower temperatures and moist conditions can improve bacterial survival as noted by their persistence in surface soils with the passing of the seasons. Some soil microorganisms can survive better in finer-textured soils, which have increased water-holding capacity.

Bacteria can be retained in soil pores due to their size and attraction to soil particles. Soils containing clays have finer textures and small pores that are more effective in physically limiting the movement of bacteria. In addition, bacteria surfaces usually carry a net negative charge that enhances their retention in soils. Cations can be attracted to the negative charge of the bacteria as well as clay mineral surfaces causing the bacteria to be retained by the soil, a process known as cation bridging. Acidic conditions increase the number of positively charged sites on colloids and these reduce bacterial movement in soils. On the other hand, dissolved organic constituents can reduce bacterial retention by soils and can promote bacteria movement. Therefore, factors including temperature, moisture, organic matter content, and predatory microorganisms have the greatest influence on survival of beneficial and deleterious soil microorganisms.

Movement of soil microorganisms is influenced by a number of other soil factors. Their movement is often enhanced in saturated soil water conditions as compared to soils that are unsaturated. The faster the flow rate (e.g., high infiltration and permeability), the greater soil microorganisms can be transported. Coarse-textured soils with low clay contents generally have high infiltration and permeability rates that will enhance microbial movement. Virus movement is also controlled to a large degree by the same factors that affect movement of soil microbes, particularly bacteria. As noted above, soil texture is extremely important as are water flow rates. Under conditions that result in movement of soil pathogens, contamination of the surrounding soils and waters can occur.

3.5.2.2 Soil Pathogens

Problems associated with *pathogenic* (e.g., disease-causing) *bacteria*, *viruses*, and *parasites* are the result of improper disposal of household and commercial wastewaters (Bitton, 1999). For example, septic systems contain wastewaters that often have large numbers of pathogenic microorganisms. Septic effluents are discharged into a drainage field where pathogens enter the soil environment. When working properly, septic tank and drainage field biological, chemical, and physical processes reduce the pathogens to safe levels; however, improperly designed systems can result in pathogen contamination of the surrounding soils as well as surface waters and groundwaters. Exposure to pathogens through drinking or eating contaminated waters and foods, respectively, can result in illness or even death. In the United States, groundwater contamination due to pathogenic viruses from septic systems has been suggested to be the leading cause of waterborne illnesses. The bacteria, *Salmonella typhi*, that causes typhoid fever has been detected in drinking waters contaminated by septic effluent.

Bacteria and virus survival in soils is highly dependent on temperature and moisture. Colder temperatures and higher soil moisture levels enhance their persistence. Bacteria and viruses associated with larger organic septic particles may be retained in soils due to physical constraints. However, since both bacteria and viruses are generally not sorbed in sandy soils, their movement may result in offsite contamination particularly during high rainfall periods. Competition among soil biological communities may destroy pathogenic microorganisms. Certain grazing protozoans can consume pathogens, as well as other microorganisms, and bacteria and fungi may produce extracellular enzymes that break down pathogenic cellular constituents.

There are several important conditions that should be considered to minimize *pathogen contamination* from septic systems. Always locate drainage fields in fine- to medium-textured soils with good permeability. Maintain an unsaturated zone between the drainage field and groundwater to prevent saturated water conditions that enhance the movement of pathogenic microorganisms. Always keep the septic system isolated from drinking water wells, surface waters, and topographic lows that may create problems from seepage. Permits are required for installation of septic systems, which include the inspection of the site and soils to identify potential problems that may result in offsite movement of pathogenic bacteria and viruses and to minimize any health risks.

3.6 SOIL DEVELOPMENT AND LAND USE

Soils are described based on their morphological characteristics. Soils contain layers, approximately parallel to the land surface, called *horizons*, that are distinguished from one another by differences in texture, color, structure, or other chemical or physical properties that set them apart from the other horizons. Horizons can be formed from the loss (eluviation) of material such as organic matter, clay, or Fe, and Al, or from the accumulation (illuviation) of these constituents.

Several *soil classification systems* are used throughout the world. The one used in the United States, and several other countries, is *Soil Taxonomy*, which was developed by the U.S. Department of Agriculture (Soil Survey Staff, 1999; 2004). Soil Taxonomy was designed to group soils according to morphological characteristics and environmental properties such as diagnostic horizons, soil texture, soil structure, soil color, soil mineralogy, soil moisture regime, and soil temperature regime. It is a hierarchical system that contains six categories of classification ranging from a general grouping of all soils to a more specific, highly detailed grouping. The six categories, listed according to increasing detail, are order, suborder, great group, subgroup, family, and series.

Soils with similar types of *diagnostic horizons* (Table 3.8) are classified into 12 *soil orders* (Table 3.9). Knowing the soil order provides a general picture of what morphological and possible chemical and physical properties a soil possesses. The more detailed categories in Soil Taxonomy provide more specific information about the soil. The family name of a soil is the most useful for direct interpretation of the properties of the soil and the environment where it is located. Soil series are subdivisions of families, and are distinguished based on specific profile characteristics.

Soil survey reports (Figure 3.11) are valuable sources of information for land-use planning. They contain information that can help make land-use decisions for agricultural and nonagricultural purposes. In addition to delineating soil by map units, soil surveys contain detailed information for land-use decision making regarding the management of soils, croplands, woodlands, recreation areas, and wetlands. Soil surveys are also useful for evaluating soils for their suitability for irrigation and their drainage potential. Limitations for various land uses are listed in interpretive tables. These tables, along with the soil description, are a necessity for initial planning of waste disposal sites such as for septic tanks, sewage lagoons, and sanitary landfills.

Geographical Information Systems (GIS), which have recently been broadened to include geographic information science, have been applied to land management decisions by using the data layers and database information to query for specific characteristics and properties that may be beneficial or detrimental to a particular land use. A GIS can compile, store, and retrieve spatially derived information that can be used to identify or explore specific environments or relationships within a geographic region, analyze data for decision making, provide data for application-specific models, and produce visual and numerical outputs for planning efforts. Data layers that can be developed and retrieved for future use include soils, vegetation, climatic conditions (e.g., precipitation and temperature parameters), water bodies, land-use type, topography (e.g., *digital elevation models*, DEMs), and others that have spatial coordinates. *Land-use planning* and *precision farming* are two areas that utilize GIS. Precision farming also relies on *global positioning systems* (GPS) to determine the exact location within a field for quantitative applications of such materials as fertilizers, liming products, animal manures, municipal biosolids, and other organic by-products.

3.6.1 Soil Morphology and Classification

Soil horizons are described, first, by a *master horizon designation* using the capital letters O, A, E, B, C, or R and, second, according to the soil horizon characteristics, by a *subordinate designation* (Table 3.8). Surface horizons are classified as either O or A horizons depending on their organic matter content. In highly eroded areas where soil surface materials have been removed, E, B, C, or R horizons may be exposed. Soils with E horizons are very common in forest soils. The E horizon is usually located below the O or A horizon, and forms as a result of the loss of

Table 3.8 Diagnostic Horizons, Designations, and Their Properties; Diagnostic Horizons Are Used to Classify Soils at High Levels of Soil Taxonomy

Diagnostic Horizon	Designations	Properties
Epipedons		
Ochric	A	Light-colored, low organic matter that does not meet criteria of other epipedons
Mollic	A	Thick, dark-colored, well-structured with high base saturation >50%
Umbric	A	Similar to mollic but with low base saturation <50%
Melanic	A	Like a mollic except developed on volcanic tephra
Anthropic	A	Anthropogenic mollic-like horizon high in P
Plaggen	A	Anthropogenic thick horizon (>50 cm) developed from long-term manure applications
Histic	O	Organic horizon formed in poorly drained areas
Subsurface Horizons		
Argillic	Bt	Accumulation of silicate clays as evidenced by clay films
Agric	A or B	Accumulation of organic matter, clay, or silt below the plow layer
Albic	E	Light-colored exuvial horizon which has lost organic matter and clays
Calcic	Bk	Accumulation of calcite (CaCO_3) or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)
Cambic	Bw	Weakly developed horizon
Duripan	Bm	Hardpan due to cementing with silica
Fragipan	Bx	Weakly cemented, brittle layer
Gypsic	By	Accumulation of gypsum
Natric	Btn	Argillic horizon high in sodium having columnar or prismatic structure
Oxic	Bo	Highly weathered horizon with accumulation of Fe and Al oxides and nonexpanding silicate clays
Petrocalcic	Bk	Cemented calcic horizon
Petrogypsic	By	Cemented gypsic horizon
Placic	B	Thin cemented plan that is black to red and held together by Fe, Mn, and/or organic matter
Salic	Bz	Accumulation of salts
Sombic	B	Accumulation of organic matter low in base saturation
Spodic	Bh, Bhs, Bs	Accumulation of organic matter and sesquioxides
Sulfuric	B	Highly acid soil with sulfur-containing mottles

considerable amounts of organic matter, clay, or Fe and Al compounds (sesquioxides). An E horizon is generally lighter in color than the horizons above and below. Horizons that have accumulated constituents translocated from the horizon above are called B horizons. Parent material, the geologic material from which the soil has formed in, is designated a C horizon. Unconsolidated rock is classified as an R horizon. In addition to the five master horizons described above, examination of some soils indicates there are some horizons that appear to have characteristics similar to the horizons above and below. These are called transitional horizons and are designated by two capital letters such as AB or E/B.

Table 3.9 Twelve Soil Orders and Their Diagnostic Features According to Soil Taxonomy

Soil Order	Common Diagnostic Horizon	Diagnostic Features
Alfisol	Argillic/Natric	Base saturation >50%; no mollic, oxic, or spodic
Andisol	Melanic/Ochric with andic properties	Volcanic ash–derived soil; noncrystalline or poorly crystalline minerals
Aridisol	Ochric plus Calcic	Dry soil; argillic, cambic, or natric common
Entisol	Ochric no diagnostic subsurface horizons	Nominal profile development
Gelisol	Histic/Ochric with permafrost	Must have permafrost within upper 100 cm
Histosol	Histic	Organic soil; peat or bog
Inceptisol	Cambic	Few diagnostic features; ochric or umbric horizons common
Mollisol	Mollic	Dark soil with high base saturation; no oxic or spodic
Oxisol	Oxic	Highly weathered; no argillic or spodic
Spodosol	Spodic	Accumulation of organic matter and sesquioxides; albic horizon common
Ultisol	Argillic	Base saturation <50%; no oxic or spodic
Vertisol	Ochric/mollic	Contains high amounts of swelling clay causing deep cracks when dry

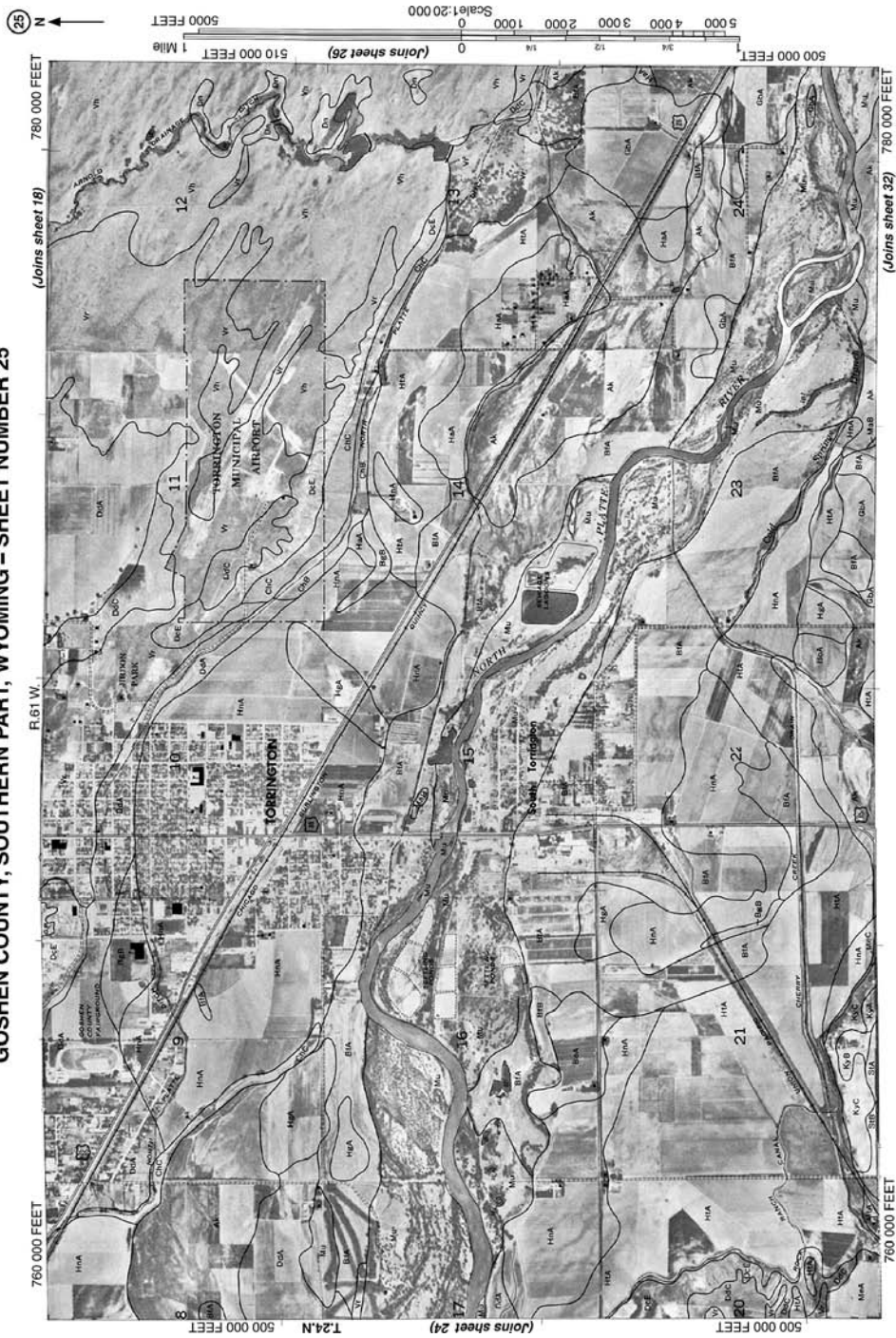
Horizons are further subdivided to differentiate the major properties or characteristics that set them apart from other horizons. The use of the *subordinate designation* allows us to distinguish, for example, a B horizon that has accumulated clay material (Bt) from a B horizon that is only weakly developed (Bw) (Table 3.8). Not all subordinate designations are used with each of the master horizons. When describing the O horizon, the decomposition state of the organic matter should always be determined to classify the horizon correctly as an Oa, Oe, or Oi, which represent sapric, hemic, and fibric materials, respectively. These three subordinate designations are reserved solely for organic horizons. The subordinate designation p (plow layer) is only used with the master horizon letter A. Most of the subordinate designations are used to classify B horizons further. It is relatively easy to determine which of the lowercase letters are used for B and sometimes C horizons because they represent processes of accumulation or changes from the geologic parent material of the soil.

The initial step in classifying soils is to determine the *diagnostic horizons*. Diagnostic horizons are of two groups: epipedons — those that form at the soil surface — and subsurface — those that form below the soil surface (see Table 3.8 for horizon designations and properties). Of the seven epipedon horizons listed in Table 3.8, only one, the histic epipedon, which is designated as an O horizon, is composed primarily of organic matter. Of the 17 subsurface diagnostic horizons, the argillic, albic, cambic, and spodic horizons are common to soils in humid regions of the United States and Canada. Soils in arid parts of the United States often have one of the following diagnostic subsurface horizons: calcic, gypsic, natric, or petrocalcic. Knowledge of diagnostic horizons is essential for classifying soils.

3.7 SOIL QUALITY

Soil quality was defined by the *Soil Science Society of America* (SSSA, 1995) as “The capacity of a specific kind of soil to function within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water quality, and support human health and

GOSHEN COUNTY, SOUTHERN PART, WYOMING – SHEET NUMBER 25



Photobase from 1966 aerial photographs. 5000-foot grid ticks based on Wyoming plane coordinate system, east zone, 1927 North American datum.

Figure 3.11

Example of a map sheet taken from the Soil Survey of Goshen County, Wyoming. The mapping units listed on the map represent the type of soil association, which is a landscape that has a distinctive pattern of soils, and slope of the area. For example, the city of Torrington is located primarily on map unit H1A, which represents Haverson and McCook loams on 0 to 3% slopes. (From Soil Survey of Goshen County, Wyoming, Southern Part by F. Stephens, E. F. Brunkow, C. J. Fox, H. B. Ravenholt, USDA Soil Conservation Service in Cooperation with the Wyoming Agricultural Experiment Station.)

habitation.” The SSSA conceptualized soil quality as “a three-legged stool, the function and balance of which requires an integration of three major components — sustained biological productivity, environmental quality, and plant and animal health” (Karlen et al., 1997). The *National Research Council* (1993) proposed a similar definition: “Soil quality is the capacity of the soil to promote the growth of plants, protect watersheds by regulating the infiltration and partitioning of precipitation, and prevent water and air pollution by buffering potential pollutants such as agricultural chemicals, organic by-products, and industrial chemicals.” Unlike “clean water” and “clean air,” however, the concept of “clean soils” and soil quality is rather new, often highly controversial, and not as well defined from a scientific perspective.

3.7.1 Assessment of Soil Quality

By defining soil quality we begin to establish the parameters that are important when we manage soils. The obvious implication is that we wish to avoid land management practices that damage soil quality and thus negatively affect the capacity of soils to function as we believe they should. Recently, there has been a great deal of interest in developing specific “indicators” — measurable or observable soil properties and processes that together characterize the present quality of a soil. These indicators would be a means to assess quantitatively the extent of soil degradation from past activities (human and natural) and also serve as a means to track the success of our efforts to restore soil quality by improved management practices. Some indicators of agricultural soil quality, such as soil fertility testing, have been used for decades, as described in Chapter 4.

However, defining soil quality conceptually, let alone quantitatively, is a complex task. Some have argued that we should assess soil “health” in much the same manner as physicians evaluate human health, using the following six-step process: (1) identify symptoms; (2) identify and measure vital signs; (3) make a provisional diagnosis; (4) conduct tests to verify the diagnosis; (5) make a prognosis; and (6) prescribe a treatment. Inherent to such an approach is the presumed ability of those who manage soils to integrate whatever quantitative indicators of soil quality can be developed with more qualitative concepts such as diagnosis of symptoms and prescription of treatments.

If we are to follow such an approach, we will need a *minimum data set* (MDS) of measurable soil quality indicators that can be used to provide quantitative information on the capacity of a soil to function in a desired manner (Table 3.10 and Figure 3.12). To have value, soil quality indicators must be clearly shown to be well correlated with quantifiable soil functions, must respond in a measurable way to external change (natural or anthropogenic), must be adaptable for use by individuals with a range of backgrounds and skills, must be found in existing databases that are accessible and of value to soil quality assessment, and must be easily integrated into larger, ecosystem-scale models, including socioeconomic models.

Figure 3.13 shows a graphical representation of a number of soil quality indicators that could be measured at a given site. Each indicator has an optimum range of values (e.g., soil pH between 6 and 8) that can be scaled to each spoke on the wheel. The innermost circle represents the minimum of the range of optimum values for each parameter, and the next circle represents the maximum. When the data for a site are plotted we can quickly surmise the number of parameters that are in or out of the optimum range.

Some have suggested that we can develop a “soil quality index” (SQI) using “pedotransfer functions” (mathematical functions that relate parameters in the MDS to broader physical, chemical, and biological processes). We might, for example, develop a pedotransfer function that uses soil texture and organic matter content to estimate hydraulic conductivity or use data on soil bulk density, water-holding capacity, and pH to estimate crop rooting depth. By combining and integrating *pedotransfer functions* with societal goals, we can separate soil quality into several distinct components (e.g., food and fiber production vs. water quality impacts), each with a different intrinsic value. It would then be possible to weight individual components of the overall SQI based on physical and social constraints such as climate, topography, hydrology, economics, and politics.

Table 3.10 Example of a Minimum Data Set (MDS) of Soil Quality Indicators That Has Been Modified for Use with Land Application Programs Where Agricultural, Industrial, and Municipal By-Products Are Used

Soil Quality Indicators in the MDS	Rationale for Inclusion of Soil Quality Indicators in the MDS	Suggested Additions to the MDS When By-Products Are Used	Rationale for Addition of Indicators to the MDS
Physical Texture Topsoil depth Rooting zone depth Infiltration	Indicators of retention and transport of water and chemicals, soil erosion, leaching, surface and subsurface runoff, and soil productivity; also related to water availability and useful in models that seek to integrate soil, landscape, and geographic variability into soil quality	Erodibility (RUSLE) Runoff potential Leachability index Compaction Heat capacity Porosity Soil color Drainage, MHW depth	Provide more direct, quantitative measures of the potential for transport of by-products or of solutes and soil particles from by-product-amended soils to water; aid in assessing the potential for loss from soils of volatile compounds, which can affect air quality
Chemical Soil organic matter pH Electrical conductivity Extractable, N, P, and K	Define soil fertility, stability, and erosion extent, potential for N loss, biological and chemical activity, thresholds of microbial activity; useful as productivity and environmental quality indicators	CEC/AEC Sorption capacity Total, extractable, bioavailable, soluble, and desorbable nutrients and nonessential elements Environmental tests for N and P (DPS, PSNT, LCM, stalk nitrate)	Better assessment of potential of soil to retain or release elements and/or organic compounds to leaching or runoff waters; quantify buildup of elements and degree of saturation of soil sorption capacity, predict plant response to N and evaluate success of N management programs
Biological Microbial biomass C, N Mineralizable N Soil respiration	Microbial catalytic potential, repository for C and N, indications of effects on soil organic matter, measures of N supply and soil productivity, changes in biomass and total C pool	Microbial diversity Biodegradation potential in surface and subsoils Redox potential	Evaluate changes in microbial population diversity and size of various communities; assess capacity of entire soil profile to degrade organic pollutants in aerobic vs. anaerobic zones

Note: RUSLE = Revised Universal Soil Loss Equation; MHW = mean high water table; CEC/AEC = cation/anion exchange capacity; DPS = degree of P saturation; PSNT = presidedress soil nitrate test; LCM = leaf chlorophyll meter.

Source: Sims, J. T. and Pierzynski, G. M., in *Land Applications of Agricultural, Industrial, and Municipal By-Products*, J. F. Power and W. A. Dick, Eds., Soil Science Society of America, Madison, WI, 2000. With permission.

If food production is of paramount performance, as opposed to air or water quality, efforts can be made to optimize soil quality for that end; in contrast, if protection of drinking water supplies and surface water quality are high social priorities, the SQI can be weighted to require intensive soil and water conservation practices, most likely at the expense of productivity (e.g., profits, crop yields).

This approach to soil quality seems a good fit for situations where the effects of soil use and management on environmental quality are *sociopolitical issues*. Consider the use of by-products as soil amendments. Local conditions (natural, economic, and political) often dictate the degree of soil quality that is acceptable when manures, biosolids, and the like are used as soil

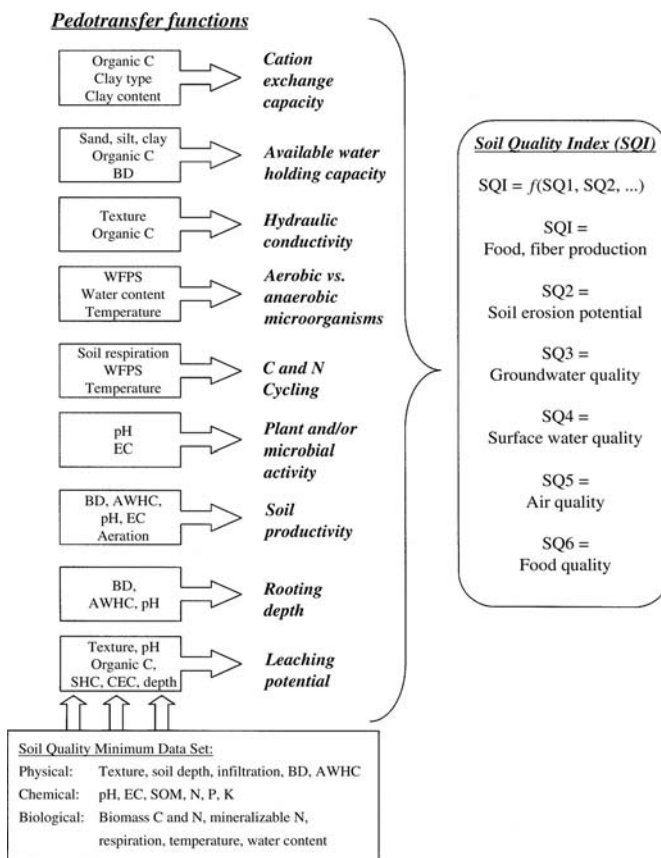


Figure 3.12 Use of soil quality indicators to assess soil processes and develop a soil quality index (SQI). (From Sims, J. T. and G. M. Pierzynski, in J. F. Power and W. A. Dick, Eds., *Land Application of Agricultural, Industrial, and Municipal By-Products*, Soil Science Society of America, Madison, WI, 2000. With permission.)

amendments, relative to other end uses for these materials. There are several reasons for this. First, if environmental protection costs are ignored, land application is almost always the least expensive approach to use (or dispose) of most by-products. Many areas do not have the economic wherewithal to implement alternatives to land application and, in some cases, such as with animal manures, this is essentially the only option, regardless of the strength of the local or regional economy. This leaves local industries, municipalities, and even state governments with no realistic options for by-product use and compels local environmental agencies to develop management programs that minimize, but usually do not eliminate, the effect of by-products on soil and environmental quality. In contrast, in some areas concerns about air and water quality are paramount and the costs of alternative uses are more willingly borne by citizens and governments. This scenario would be most common in urbanizing, economically stable areas where the public relies on more expensive technological or political solutions to deal with by-products. This may include more extensive treatment to reduce environmental risk or the development of public-supported infrastructures or policies that dispose of by-products by means other than land application. Examples include tertiary treatment at wastewater facilities, large-scale composting or pelletization facilities that are subsidized by local tax revenues to transport by-products from the area of generation to another region, and even strict zoning ordinances that prevent the growth of industries that generate by-products perceived to be offensive (e.g., the odors and by-products from poultry or swine operations) regardless of the cost to the local economy.

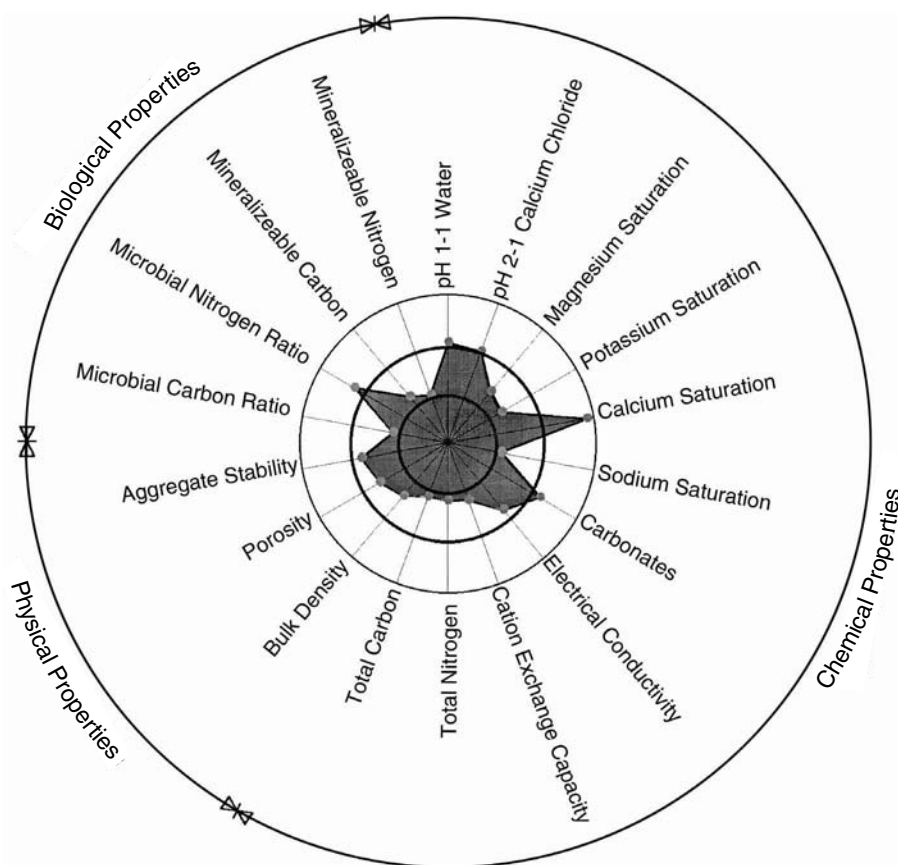


Figure 3.13 Graphical representation of select soil quality indicators for a site. The innermost circle represents the minimum of the range of optimum values for a given parameter, and the next circle represents the maximum. (From Thien, S. J., personal communication, 2004.)

Clearly, the soil quality considered desirable or acceptable will vary between these two scenarios (a lesser developed country, limited resources, with food production a high priority vs. an industrialized, wealthy country where environmental protection is a high priority). Historically, the acceptable balance between positive and negative effects of most land uses on the environment has been decided by local and state governments, within general rules and regulations established by federal agencies to protect air and water quality. It can be argued that throughout the decision-making process these governmental agencies should also include a systematic assessment of the short- and long-term impacts of land use on soil quality. In most cases decision making begins with an assessment of land-use goals for a defined geographic area. Once these goals are identified and agreed upon, the next step is to develop the *minimum data sets* and *pedotransfer functions* needed to assess, quantitatively, the impacts of desired land uses on soil quality and the subsequent risks of these land uses to other sectors of the environment. From there we can derive the broader SQIs needed to evaluate more fully how the changes in soil quality associated with land use will affect food production and safety, air and water quality, and ecosystem health. This will help us to better weight the socioeconomic and political aspects of land use that are often as influential as the scientific and technological assessments we derive from such SQIs. There is also a need to develop an approach to monitor soil quality with time, integrating advances in research, improvements in technology, and changes in the politics and economics of land use. Finally, decisions taken to improve or sustain soil quality must occur in a broad social context as they often have adverse implications for some sector of the economy

or environment. For example, political and socioeconomic considerations in soil quality assessment will be of utmost importance for land application of by-products (animal manures, municipal biosolids) because of the environmental and economic tensions that arise when restrictions to land application are proposed (e.g., P-based management of animal manures; see Chapters 6 and 8) or alternatives are discussed (incineration, landfilling, ocean dumping). Given this, efforts to assess soil quality and use SQIs as management tools must have disciplinary breadth, going beyond the soil and agricultural sciences to include, for example, economists, political scientists, engineers, hydrologists, and ecologists.

Environmental Quality Issues/Events

Using GIS to Identify Areas for Alternative Crop Production

The Bighorn Basin in Wyoming is an important agricultural region that relies heavily on irrigation for the cultivation of sugar beet, barley, alfalfa, and dry bean crops. To diversify crop production in the basin, a GIS was used to develop a soils layer for the region, create continuous data layers of several climatic variables, catalog crop growth parameters for different agricultural crops, and combine growth parameters with environmental data to display areas for possible alternative crop production. Environmental traits of the basin (e.g., soils, temperature minimums and maximums, frost-free period, growing degree-days, etc.) will dictate where various crops can be produced. Both ARC/INFO (version 7.1.2) and ArcView (version 3.1) (ESRI, Redlands, CA) were used for GIS evaluation of 28 potential alternative crops. Maps developed in this project provide basin producers with potential alternatives to current crop production practices.

Because published soil survey data were not available for a majority of the basin, a *GIS-derived soils map* was generated using regional bedrock geology, surficial geology, and elevation properties. The available soil series were related to bedrock and surficial geology combinations for predicting soils for the rest of the basin. As these soil series did not account for the entire region, other geologic combinations were applied to the soil model utilizing GIS decision rules. Based on this method, every bedrock/surficial geology combination was assigned a soil family classification and a representative soil series was assigned to each family from series currently mapped in Wyoming.

The GIS-derived soil map included 19 different soil associations, with a large proportion of the land classified as Torrifluvents. Most of the irrigated agriculture in the Bighorn Basin is located in Torrifluvents. Soils in the area that are not suitable for crop production include those that are frigid, have high shrink-swell tendencies, possess too low a water-holding capacity, or are shallow to bedrock. The remaining soils are suitable for crop production (soils that are deep or have a texture conducive to plant growth) and represent 62% of the study area. The lowland areas comprise soils typically under agricultural production, while higher elevation soils are generally used for livestock grazing and timber harvesting. Creation of the soil data layer allowed for the use of textural classes in an alternative crop analysis.

The 18 weather stations existing in the basin have collected weather data for 30 years or longer. The climatic parameters recorded at these sites were extrapolated to predict conditions throughout the area. Using *geostatistical techniques*, the weather station locations and attributes were used to create continuous weather patterns for the basin. Sample variograms were created for each of the climatic variables to determine the model that could optimize the data. Model parameters such as nugget, sill, and range were estimated, and cross-validation was performed to check the accuracy of the model selected. Once the correct model and parameters were chosen, *kriging* was performed to estimate the unsampled points. The climatic data were interpolated using the spline method to create 31 continuous GIS data layers that represented the Bighorn Basin climatic conditions. Examples included growing degree-days, June maximum temperature, and 90% chance of frost-free period. Climatic variable contour maps were related to basin topography; i.e., with an increase in elevation there were decreases in frost-free period, growing degree-days, and temperature, but there was an increase in precipitation. Basin elevation gradually increases from east to west.

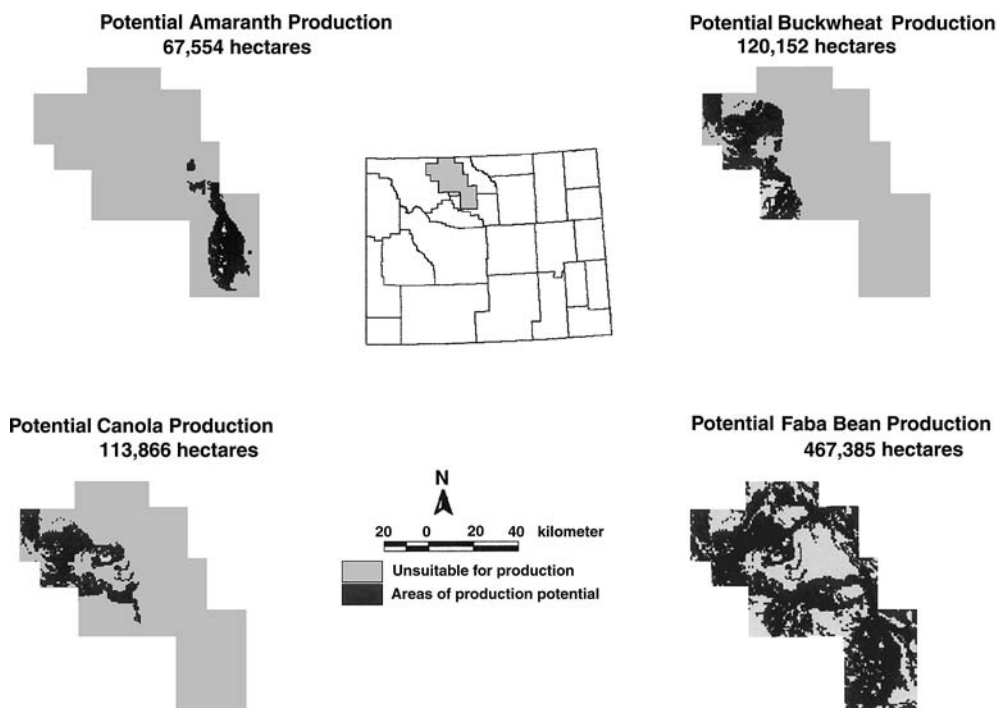


Figure 3.14 Potential production areas for the introduction of alternative crops, amaranth, buckwheat, canola, and faba bean in the Bighorn Basin, Wyoming.

General *growth requirements* for the different alternative crops were compiled and cataloged in a GIS format. Because specific crop variety information was unavailable, the growth parameters for each crop were a broad categorization of what each species would require for growth and development. Once the data were compiled into the GIS, analyses were performed using the GIS map algebra protocol. The parameters queried included such items as soil texture, length of *frost-free season*, maximum July temperature, minimum September temperature, and *growing degree-days*. Areas with the desired crop growth parameter combinations for each crop were identified and displayed as maps illustrating potential areas for *alternative crop production*.

Examples of areas suitable for the production of amaranth, buckwheat, canola, and faba bean are shown in Figure 3.14. Eight of the alternative crops modeled (amaranth, chickpea, onion, quinoa, safflower, sesame, sorghum, and sunflower) may potentially be cultivated in the eastern part of the basin. This is the warmest area and has the longest frost-free period. These crops require more heat to develop than the cool-season crops. Broccoli, buckwheat, canola, carrot, cauliflower, crambe, Kentucky bluegrass turf seed, leek, lentil, lettuce, mint, and radish are cool-season crops that prefer less heat during the growing period. Because of this preference for cooler temperatures, production of these crops may be possible in the western portion of the basin. Finally, eight of the crops investigated (asparagus, beet, cabbage, cowpea, field pea, faba bean, medic seed, and tall fescue turf seed) can potentially be cultivated throughout the area on suitable soils. This is due to the broad temperature range to which these crops are adapted.

GIS provides an excellent means for exploring the possibilities of cultivating new or alternative crops. The process of locating areas suitable for growth is rapid, once the necessary information is entered into the GIS database. Crop diversification is important for environmental and economic reasons. However, before attempting the cultivation of alternative crops, additional parameters relating to the exact variety to be grown should be thoroughly investigated.

— Source: Young J. et al. (2000)

PROBLEMS

- 3.1 You are invited to give two presentations, one to a group of elementary school children and another to your state legislators. The topic of your presentation is “Soil Environmental Quality.” You are asked to describe first the meaning of soil so that everyone will understand your definition of soil. Write a brief description of what you would present to both groups. Would you define soil differently to both groups, and, if so, why?
- 3.2 Why is it important to understand soil properties and functions to evaluate environmental quality issues and events that pertain to different ecosystems?
- 3.3 Determine the textural class of soils that contain:

a. 25% sand	25% silt	50% clay
b. 50% sand	25% silt	25% clay
c. 75% sand	15% silt	10% clay
d. 25% sand	50% silt	25% clay
e. 33% sand	33% silt	34% clay

What would be the textural class of these soils if each contained 5% organic matter?

- 3.4 Calculate the mass of soil (in kg) in 1 ha (10,000 m²) to a depth of 1 cm and a bulk density of 1.35 Mg/m³. Repeat this calculation for a 15-cm depth.
- 3.5 A soil contains 50 mg/kg Zn. Calculate the mass of Zn in 1 ha of soil to a depth of 15 cm assuming a bulk density of 1.35 Mg/m³. Develop an equation that converts the concentration of a substance in soil (in mg/kg) to mass per hectare (in kg/ha) as the soil depth varies (in cm).
- 3.6 Describe the relationship between particle density and bulk density. How do these soil physical properties influence (a) the movement of water; (b) plant growth; (c) wind and water erosion; and (d) environmental quality?
- 3.7 Determine Freundlich (K_f and $1/n$), Langmuir (K_1 and b), and IM (m , b , and RSP) parameters for the following soil SO₄²⁻ adsorption study. For this experiment, 5 g soil and 50 mL solution were used. Explain the data.

Initial SO ₄ ²⁻ (mg/L)	Equilibrium SO ₄ ²⁻ (mg/L)
0	2.0
5.0	5.5
10	9.0
20	16
40	30
80	58

- 3.8 How does soil organic matter affect the physical, chemical, and biological properties of soils? Explain the relationship between soil organic matter and (a) soil structure; (b) ion-exchange capacity; and (c) microbial activity.
- 3.9 What soil properties can influence the mobility of contaminants that could degrade surface-water and groundwater systems?
- 3.10 Describe three physical, chemical, and biological processes involved in soil development. Indicate the importance of each of these soil processes.
- 3.11 Why is a soil survey a valuable resource when considering the purchase of a building site, location of a septic system, production of a new or alternative crop, and implementation of a wildlife reestablishment program?
- 3.12 Describe how land-use planning and GIS can be used to assist a city, county, or state in governing the proper use of certain areas for agricultural production, landfills, wastewater treatment facilities, road construction, recreational areas, and long-term sustainable approaches to population growth and economics.

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CHAPTER 4

Environmental Testing: Soils, Waters, Plants, Wastes, Organics

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4.1 INTRODUCTION

There are a variety of media that may require sampling or assessment for agronomic and environmental purposes. These include soils, waters, plants, air, and various by-products that may be applied to soils or that are present in the environment. Often an analysis is designed to determine the concentrations of contaminants or plant nutrients in a media sample. Other analyses determine basic chemical (e.g., pH or electrical conductivity), physical (e.g., soil bulk density), or biological (e.g., soil respiration, biological oxygen demand) properties that can, for example, be indicators of the suitability of soil for plant growth, or the suitability of water for human consumption or irrigation.

From an agricultural perspective, we should know the specific components of a successful soil testing program that apply to land-use programs where plant growth or crop yields are of greatest interest. However, from an environmental view, we must also be able to evaluate some specific considerations that relate to soil, water, and by-product testing where protection of human health and environmental quality are the primary concerns. In addition to soil and water quality issues, plant analysis has become a useful technique for interpreting nutrient levels in vegetation. Use of soil amendments for agriculture and land reclamation operations has also gained in popularity because of the beneficial properties these materials can provide, including nutrients, organic matter, pH buffering, as well as other chemical, physical, and biological contributions. There is also increasing interest in the concentrations of various constituents in air. This interest is driven by concerns about air quality, global climate change, and acidic deposition. Some of the constituents of interest are dust ($\text{PM}_{2.5}$ or PM_{10}), ammonia, NO_x , SO_2 , N_2O , CH_4 , and CO_2 . This chapter covers information on the rationale, procedures, and interpretation involved in environmental testing of soils, waters, plants, air, and by-products.

Total concentrations of various elements of interest can be determined in any media. This can be accomplished in a variety of ways including digestion in strong acids followed by analysis or by some direct technique that may or may not cause sample destruction. Total elemental concentrations can be very useful but often are of little value. For example, total lead (Pb) concentrations in soil are sometimes used to as a screening tool to predict potential problems from human exposure to soil Pb, but are in fact a poor predictor of the actual human health risk from soil Pb (see Chapters 1 and 9 for discussions of soil Pb bioavailability). Similarly, total nutrient concentrations in soils are poor predictors of the probability of a crop yield response to fertilizer additions. Therefore, attempts are made to either measure a subfraction of the total amount of an element in a sample, e.g., extractable phosphorus (P) rather than total P in soil, or to measure the concentration of a particular molecular species of an element, e.g., nitrate (NO_3^-) in water rather than total nitrogen (N). This is an important and often confusing concept and we must be certain we understand what has been measured in a particular analysis. The basic idea is to measure a fraction that provides us with information more useful than that obtained from total elemental concentrations.

The concept of measuring a subfraction of an element is related to bioavailability. Bioavailability for soils was defined in Chapter 1 as the subfraction of the total amount of a substance in a soil that can cause an effect, positive or negative, on an organism. The same definition could be extended to include air and water as well. From this, we might conclude that a measured subfraction of an element in soils provides an estimate of the bioavailability of that element. This is true in some situations although semantics becomes an issue. Some would argue that only an organism can be used to measure bioavailability and that data from procedures such as soil extractions should be called bioaccessible, or plant available, rather than bioavailable. Others use bioavailable to describe any subfraction that predicts a response by an organism.

The situation with organic chemicals is more complicated than that for elemental analysis. There are no procedures for measuring the total concentration of a specific organic chemical in matrices such as soils, by-products, or a water sediment mixture. Digestion procedures would likely degrade the organic chemical and are not suitable. In general, the organic chemicals must be brought into a solution phase through an extraction procedure prior to analysis.

Often the measured concentration of all or a portion of a substance or element in a media sample is given a very specific name such as soluble, organic, or bioavailable. These names often imply a more specific chemical form than is actually warranted. For example, from a chemistry perspective, the term soluble would imply an element that exists only as individual ions in solution (e.g., Zn^{2+} or H_2PO_4^-). For water analysis the term soluble actually refers to the measured amount of a substance or element after the sample has been passed through a $0.45\text{-}\mu\text{m}$ filter. Some of the element or substance may be soluble in the chemistry sense, but some will be associated with small mineral or organic matter particles that also pass through the filter. Thus,

“soluble” for a water sample is an operationally defined fraction; that is, a fraction measured by a particular procedure.

Proper *quality assurance/quality control* (QA/QC) procedures must be followed for sampling and analysis of all environmental media. The process begins at the point of collection where critical information should be recorded (location, date, time, personnel, etc.) and a chain of custody established. The chain of custody should provide information on storage location and conditions of a sample at all times as well as the names of individuals who have handled or transferred the samples. To appreciate the importance of a complete record of chain of custody, consider an environmental media sample collected as part of a criminal investigation, an unusual but not unheard of occurrence. Any breaks in the chain of custody record could be exploited by the criminal defense team as a means of introducing “reasonable doubt” as to the validity of any analyses of the samples. Improper storage may affect results and insecure storage implies opportunities for tampering with evidence. Other features of a proper QA/QC plan include provisions to identify contamination from glassware or reagents, and acceptable instrument performance for individual runs as well as across multiple runs.

4.2 AGRONOMIC AND ENVIRONMENTAL TESTING PRACTICES FOR SOILS

Soil testing has been defined as “rapid, chemical analyses to assess the plant-available nutrient status, salinity and elemental toxicity of a soil” (Peck and Soltanpour, 1990). Soil testing includes not only the actual analyses of soils but also the interpretation of the results and the development of recommendations for an increasingly diverse variety of land management programs including, but not limited to, production agriculture, horticultural practices (e.g., golf courses, parks, and other landscaping activities), homeowner needs such as gardens and lawns, and disturbed land reclamation. In practice, soil testing is probably one of the most successful applications of the basic principles of soil science to all forms of land management.

A comprehensive soil testing program has four basic components:

1. Soil sample collection and handling
2. Soil chemical, physical, or biological analysis
3. Interpretation of the analytical results of the soil test
4. Development of economically and environmentally sound recommendations for lime, fertilizers, and other soil amendments

Acceptance and successful use of soil testing requires a basic understanding of how each component of a soil testing program can influence the resulting recommendations. Users of soil testing must also realize that results of a soil analysis (or any environmental material tested) are only as good as the samples evaluated, as well as the information used for predicting soil–plant correlations. In many instances, problems with soil testing are not due to analytical errors or unreasonable recommendations, but to inappropriate sampling or unrealistic expectations of what can be learned from a soil test.

4.2.1 Soil Sample Collection and Handling

Collection of a soil sample that is representative of the entire area of interest, whether it is a cropped field, a pasture, rangeland, golf course, a lawn or garden, or even severely disturbed soils at construction or mining sites, is the most important step in any soil testing program. A high degree of natural variability in soil chemical, physical, and biological properties can exist even within a very small area and create differences that may have marked effects on plant growth. *Soil management practices*, such as the method of fertilizer or animal manure application, the type of

tillage operations used, and even the year-to-year selection of what plants will be grown, can further contribute to the spatial variability in soil testing results. Understanding the nature of this spatial variability is the first step in collecting a soil sample that truly represents the area of interest.

A careful assessment of the soil types present and a thorough review of past management activities that might affect the soil properties measured in a soil test are thus prerequisite steps in the determination of the number of separate soil samples required at a site. Areas that are very different in soil type, which have been managed or cropped differently, or that clearly have some type of problem with plant growth should be sampled separately. While collection of multiple soil samples is time-consuming and costly, it is the best way to estimate nutrient needs accurately for a large area containing different soils or for areas that will be subdivided and used for different purposes.

The proper time of year to collect a soil sample and the frequency of soil sampling should also be considered carefully. Soil samples can be collected at any time of the year that the ground is not frozen. Routine soil tests for lime and fertilizer recommendations should be performed from 3 to 6 months prior to planting. This usually provides sufficient time for management decisions based on the results of the soil test to be made and implemented in a timely manner. For example, if a soil test recommends that limestone is needed to correct a problem with soil acidity, it is important to know this several months in advance of planting because of the time required for the limestone to react in the soil and raise the soil pH to the desired value for the plants to be grown. Soil testing well in advance of planting also allows time to change the type of plants to be grown if soil test results indicate that growing conditions are inappropriate for the plant or plants initially selected for the site, such as when saline (e.g., salt) or possibly sodic (sodium, Na) affected conditions are present. The frequency of soil testing varies somewhat with the plants to be grown and the nutrient management practices used. With production agriculture, soils ideally should be sampled at the same time of year (e.g., spring or fall) and at 2- to 3-year intervals. Sampling at the same time of year minimizes the effect of natural seasonal variations on soil pH and plant nutrients.

Once the areas to be sampled have been identified, the next step in soil sampling is to determine the appropriate depth to sample. This decision depends on the type of soil test to be performed. Soil samples for routine soil tests of plant-nutrient availability and lime requirement are usually obtained from the “topsoil,” typically the top 15 to 20 cm of the soil. Some important exceptions to this general rule are soil nitrate tests (see Chapters 5 and 8), soil samples to estimate the effect of pH on herbicide activity in no-till cropping systems (0 to 2 cm), samples from pastures (0 to 10 cm), and, in certain situations, samples from subsoil horizons. When collecting subsoil samples, care should be taken to minimize contamination of the subsoil sample by topsoil. Such contamination can seriously influence the results obtained. In all cases it is important to ensure that the sample is collected at the appropriate depth. Sampling too deep or too shallow may lead to inappropriate conclusions about the distribution of a nutrient or nonessential element in the soil profile, and lead to inaccurate soil management recommendations.

4.2.2 Methods of Soil Analysis

Soil analysis in the laboratory is the most accurate and reproducible step in soil testing. Standard techniques for sample handling, preparation, and processing, as well as a regular program of QA/QC, ensure that instruments are running properly and that analyses are performed reliably each time. Numerous publications describe the analytical methods used by soil testing laboratories in detail (see the Supplementary Materials section of this chapter). When soil samples are received by the soil testing laboratory, they are usually dried, ground, thoroughly mixed, and sieved to remove any particles larger than 2 mm in diameter. A typical “routine” soil test is then conducted, which usually includes soil water pH, lime requirement, organic matter content, and “available” soil nutrients, e.g., P, potassium (K), calcium (Ca), magnesium (Mg), manganese (Mn), and zinc (Zn), as determined by a chemical extraction process.

Soil test “extractants” are typically dilute solutions or mixtures of acids, bases, salts, and chelates. Biological techniques (e.g., bioassays based on microbial growth) have been used but are generally too expensive and time-consuming for routine use. The most effective concentrations and relative proportions of the reagents in a chemical extracting solution were usually determined empirically by comparison of the amount of an element extracted from the soil with some type of biological response (e.g., yield) by a target organism (e.g., plants). The nature of the chemical solutions used in soil testing is illustrated by comparing three different extractants: the Mehlich 1 soil test, which is a dilute mixture of two strong acids ($0.05\text{ M HCl} + 0.0125\text{ M H}_2\text{SO}_4$) used in the southeastern and mid-Atlantic United States; the AB-DTPA soil test, which is a dilute combination of a base ($1\text{ M NH}_4\text{HCO}_3$) and a chelating agent (0.005 M DTPA) used in the western United States; and the Bray P1 soil test, which is a dilute mixture of a strong acid (0.025 M HCl) and a complexing ion ($0.03\text{ M NH}_4\text{F}$) used in the midwestern United States. All tests are well accepted, but their use should be confined to the regions where research has shown them to be accurate.

Soil testing extractants developed for plant nutrients have also been used to assess the risk of plant uptake of nonessential elements, but have only been partially successful. Other soil testing methods are also used for these elements, although not to measure biological availability. Examples include measuring total sorbed metals to monitor the accumulation of elements in the soil up to some defined regulatory limit and use of the *toxicity characteristic leaching procedure* (TCLP) to determine if a soil is sufficiently polluted with an element or organic compound to be considered a hazardous waste. Recent advances in environmental soil testing for some metals, i.e., cadmium (Cd), Pb, Zn, have used extracting solutions that simulate the biological activity within the human digestive system, referred to as the physiologically based extraction test (PBET).

Many other chemical, physical, and biological soil tests are available to characterize the suitability of soils for various land uses. Readers are referred to *Methods of Soil Analysis* (Sparks, 1996) and *Soil Sampling and Methods of Analysis* (Carter, 1993) for a thorough discussion of available soil testing methods and analytical methods that are widely used.

4.2.3 Soil Testing Interpretations and Recommendations

Interpretation of soil testing results is a process by which the analytical results of the tests are related to soil management decisions. For example, with plant nutrients the goal is to identify, based on the concentration of the nutrient in the soil, the probability of a profitable plant response to additions of that nutrient in fertilizers or other soil amendments (e.g., lime, animal manures, municipal biosolids, composts). Soil test categories (Low, Medium, Optimum, High, Very High, Excessive) relate the quantitative results of a soil test to the likelihood of a crop yield response to fertilization or manuring. Examples of the definitions of these soil test categories follow:

- *Low*: The nutrient concentration in the soil is inadequate for the growth of most plants and will very likely limit plant growth and yield. There is a high probability of a favorable economic response to additions of the nutrient.
- *Medium*: The nutrient concentration in the soil may be adequate for plant growth, but should be increased into the optimum range to ensure that plant growth and yield are not limited. There is a low to moderate probability of a favorable economic response to additions of the nutrient.
- *Optimum*: The nutrient concentration in the soil is in the range recommended for the growth of all plants. Because there is a very low probability of a favorable economic response, nutrient additions are rarely recommended.
- *Excessive*: The nutrient concentration in the soil is above the range recommended for the growth of all plants. Additions of the nutrient will be unprofitable, may have undesirable effects on plant growth, and are not recommended. Erosion, runoff, and leaching from soils that are excessive in P can have negative effects on surface water quality (see Chapters 6 and 8).

The final step in a soil testing program is the development of a *site-specific recommendation*. Plant nutrient recommendations are based not only on the soil test value for a particular nutrient, but on other pertinent factors as well. Among these are the type of plant to be grown and the realistic yield goal for that plant in a given soil, prior soil management and cropping practices (e.g., use of animal manures, municipal biosolids, composts, liming materials, legumes), the nutrient source and application technique to be used, and the potential for nutrient accumulations or losses that may create environmental problems. Most soil testing recommendations for plant nutrients follow a sufficiency level philosophy. This approach is based on the well-documented fact that a measurable “critical” soil test level exists below which responses to nutrient additions are probable and above which they are not. Soil test calibration research is used to develop the quantitative relationship between soil test values for a nutrient and the probability of a profitable crop response to additions of that nutrient. Decades of practical experience and applied research have shown that soil test-based recommendations are the most economically and environmentally efficient means to identify the need for supplemental plant nutrients. However, individuals submitting soil samples need to be familiar with the soil management process. Slight adjustments in a soil test-based recommendation in accord with the experience of the farmer, homeowner, Cooperative Extension agent, or crop consultant may be necessary and useful.

4.2.4 Environmental Soil Testing

As discussed above, soil testing has traditionally been used to evaluate the soil limitations to agronomic crop performance imposed by nutrient deficiencies, pH, soluble salts, etc., and to guide the recommendation process so that these limitations could be eliminated economically and without affecting the quality of our environment. In recent years, interest has developed in the area of environmental soil testing, defined here as “quantitative analysis of soils to determine if environmentally unacceptable levels of nutrients, nonessential elements or organic compounds are present.” Environmental soil testing is a much more ambiguous process than agricultural soil testing because it is usually quite difficult to quantify the meaning of the term “environmentally unacceptable.” Environmental soil testing lacks a clear, quantitative measure of success such as crop yield for agricultural soil testing. Therefore, the entire process of soil testing, from sample collection to recommendation, becomes more diffuse and complex. Nevertheless, the rising interest in environmental protection in many areas of the world has prompted an increased effort to use soil testing to assess the risks posed by soils to other sectors of the environment, particularly groundwaters and surface waters.

In the broadest sense, the goals of environmental soil testing are the same as those of routine, agricultural soil testing — rapid, accurate, and reproducible soil analysis by the most appropriate methods — and a reasonable interpretation of results related to environmental risk. Some factors to consider when developing an environmental soil testing program are discussed next, using two reasonably common examples, potentially toxic trace elements and plant nutrients that are known to degrade water quality. In both cases it is critical to consider the conceptual differences in interpretation of an environmental soil test, compared to an agricultural interpretation (Figure 4.1).

4.2.4.1 Soil Testing for Potentially Toxic Trace Elements

Soil testing for potentially toxic trace elements is an environmental issue because some plant nutrients — copper (Cu), molybdenum (Mo), and Zn — and nonessential elements — arsenic (As), Cd, chromium (Cr), mercury (Hg), nickel (Ni), Pb, selenium (Se) — have been shown to be toxic to plants, animals, or humans. Soils may naturally contain high concentrations of one or more of these elements (very unusual), or concentrations may increase as a result of some anthropogenic activity, such as the intentional addition of wastes as beneficial soil amendments (e.g., animal manures, municipal biosolids, industrial by-products), mining for coal, metal, phosphate (P), and

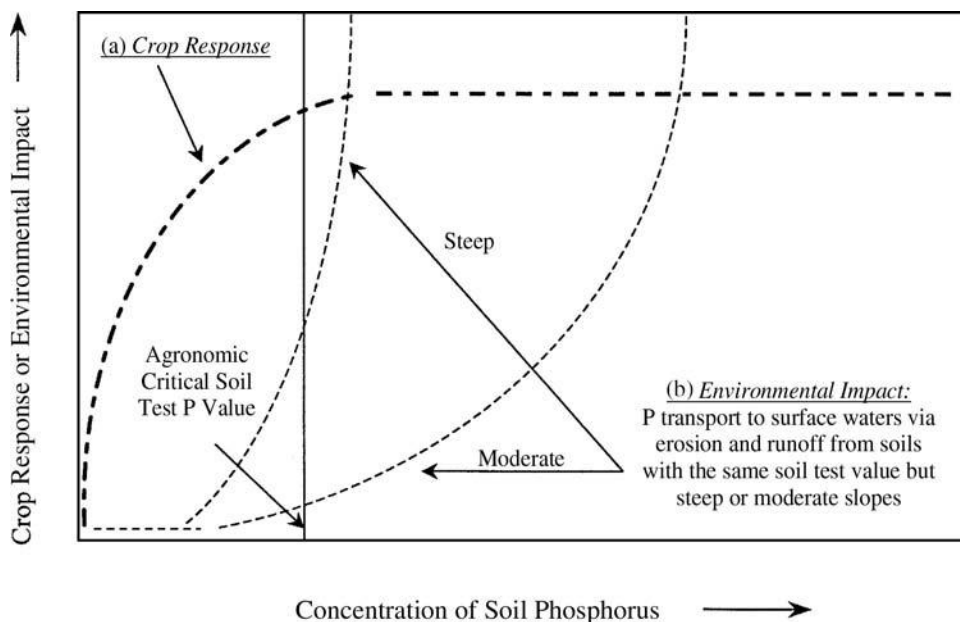


Figure 4.1 Illustration of the different nature of the relationships between the concentration of an element in the soil and (a) crop response to the element vs. (b) the potential for the element to affect the environment. In this example, the influence of soil P on water quality is affected by both the concentration in the soil and topography (slope), which influences soil, water, and P loss by erosion and runoff. (Adapted from Sims, J. T., Soil fertility evaluation, in *Handbook of Soil Science*, M. E. Sumner, Ed., CRC Press, Boca Raton, FL, 1999.)

other materials, and, in some cases, irrigating with waters containing impurities. Some soils may be highly polluted with toxic elements due to mismanagement of potentially beneficial wastes, by an accidental spill or discharge, or as a result of an industrial activity such as mining or smelting. Note that contamination and pollution are not the same. Contamination occurs when a substance is present at concentrations higher than would occur naturally but no adverse effect on an organism is apparent, whereas pollution implies not only an elevated concentration in the soil, but clearly documented adverse effects on some organism (see Chapter 1).

Soil testing for potentially toxic trace elements begins with an understanding of the nature of the risk involved — what organisms may be affected, by what pathway, and by which elements. Primary areas of general concern are direct soil ingestion, phytotoxicity, plant uptake and food chain contamination, and water pollution from erosion, runoff, or leaching (see Chapter 13 for a discussion of risk assessment). Direct soil ingestion is normally only a concern for Pb and with young children who are most likely to ingest soil or inhale dust from high-Pb soils. Phytotoxicity is rarely an issue with Pb except in highly polluted soils at industrial sites, but it is a greater concern with Cu, Cr, Ni, and Zn. Food-chain contamination and human-health effects are most often associated with Cd and Hg and water quality concerns with As, Cu, Hg, and Se. Knowledge of the nature of the risk and the element of concern helps to determine the most effective soil sampling protocol. In the case of Pb in urban soils where human health is the concern, it may be advisable to collect very shallow soil samples (<2 cm) because this is the soil depth most likely to be ingested. A similar depth would be useful if runoff or erosion is the issue considering rainfall primarily interacts with only the uppermost few centimeters of the soil surface. However, if concerns exist about groundwater pollution, sampling into subsoil horizons, perhaps to a depth of 1 to 2 m, would be recommended to determine if elemental leaching has occurred. For elements where the main concern is phytotoxicity and food-chain contamination, the normal sampling depths associated with the crops to be grown are usually acceptable (e.g., 0 to 20 cm). If remediation of the site is the

goal, by soil removal, soil washing, or soil amendment, then systematic deep sampling (e.g., 0 to 5, 5 to 10, 10 to 20, 20 to 40, 40 to 60, 60 to 100 cm) is recommended to determine the depth of soil contamination and thus the extent of remediation required. Careful consideration should also be given to the soil sample handling and preparation steps to avoid contamination from any sampling and mixing tools or grinding and sieving devices (e.g., stainless steel, used in many electric grinding devices, contains Cr and Ni) and to protect the health and safety of the individual taking the sample.

The method of analysis to be used varies with the intent of the test. If the goal is to assess biological availability (e.g., plant uptake), then many dilute acid- or chelate-based soil test extractants may be suitable, providing due consideration is given to the most appropriate test for the intended land use. However, if the goal is to quantify the extent of accumulation of an element, relative to normal soils or natural background levels, or to monitor this accumulation over time, methods that determine or approximate total elemental content are recommended. One example is EPA Method 3050 (U.S. EPA, 2004), which successively digests a soil sample with concentrated nitric (HNO_3) and hydrochloric (HCl) acids and hydrogen peroxide (H_2O_2) to measure “total sorbed metals” by acidic dissolution of clays, oxides, and carbonates and oxidation of organic matter; elements associated with silicates are not dissolved. Therefore, for a true measure of total elemental content of a soil sample, complete digestion of the soil with strong acids (e.g., HNO_3 - HClO_4 for Cd, Hg, and Pb), by carbonate fusion (Cr, Ni), or by alkaline oxidation techniques (As, Se) is required. Given the costs and difficulty of measuring total elemental content of trace elements in soils, it is often advisable to use rapid soil testing methods as surrogate monitoring techniques.

Interpretations and recommendations for soil tests for potentially toxic trace elements are considerably more difficult than for agricultural systems, and are often very site and element specific. As mentioned above, the main difficulty lies with soil test calibration — establishing a quantitative relationship between an agreed-upon measure of environmental risk and the amount of an element measured by the soil test. In most cases this has been done by the use of complex risk assessment models that first identify the “target organism” of concern (e.g., human vs. plant) and then evaluate all possible pathways by which the target organism may be exposed to the risk factor (the toxic trace element). If possible, a “most sensitive pathway” is identified, defined as the lowest soil concentration at which an adverse effect on the organism would be likely to occur (e.g., soil ingestion vs. consumption of contaminated drinking water). Regulatory upper limits may then be established for that pathway, which can be monitored by the soil testing methods described above. This approach was used by the EPA in the formulation of the national rule for the disposal and utilization of municipal biosolids, which established regulatory limits for the total amount of several trace elements that could be applied to agricultural soils (see Chapters 9 and 13).

4.2.4.2 Soil Testing for Plant Nutrients with Water Quality Impacts

Soil testing for plant nutrients that can degrade water quality is focused primarily on nitrogen (N) and P because of their well-documented effects on groundwater (N) and surface water (N, P) quality. The principles, practices, and problems of soil N management and N testing are discussed in Chapters 5 and 8. Other than the methods described in those chapters, for example, the presidedress soil nitrate test (PSNT), which focus on identifying sites with an adequate N supply and thus avoiding unnecessary applications of fertilizers or organic sources of N (animal manures, municipal biosolids), there are no other approaches currently available for use in an environmental soil testing program for N. Environmental soil testing for P, however, is a considerably different matter. Growing international concerns about the role of P in the eutrophication of surface waters (see Chapter 2) have stimulated a large research effort on environmental soil testing for P (see Chapters 6 and 8). The focus of this effort has been the use of soil testing alone, or as a component of indexes and models, to identify soils that are most likely to be significant nonpoint sources of P pollution of streams, rivers, ponds, lakes, and bays.

Example Problem 4.1

Soil samples are collected to be used for a PSNT. The equivalent of 10 g of dry soil is extracted with 100 mL of 1 M KCl. Then, 10 mL of this extract is diluted to 25 mL and the resulting solution has a NO₃-N concentration of 2 mg/L. What is the extractable NO₃-N concentration of the soil? If this soil sample represents the top 30 cm of an agricultural field, how much NO₃-N is present expressed as kg N/ha. Assume the soil bulk density is 1350 kg/m³.

$$\frac{0.1 \text{ L extract}}{0.01 \text{ kg soil}} \times \frac{25 \text{ mL diluted extract}}{10 \text{ mL original extract}} \times \frac{2.0 \text{ mg NO}_3\text{-N}}{\text{L}} = \frac{50 \text{ mg NO}_3\text{-N}}{\text{kg soil}}$$

$$\frac{1350 \text{ kg soil}}{\text{m}^3} \times \frac{10000 \text{ m}^2}{\text{ha}} \times 0.3 \text{ m} \times \frac{50 \text{ mg NO}_3\text{-N}}{\text{kg soil}} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = \frac{202.5 \text{ kg N}}{\text{ha}}$$

One approach proposed for environmental soil testing for P is simply to establish an upper critical limit for soil P using currently available agronomic soil testing methods (e.g., Bray P1, Mehlich 1, Olsen P). Soils that exceed the upper critical limit for soil test P would no longer receive P inputs from any source (e.g., fertilizers, animal manures, municipal biosolids) and would be targeted as priority areas for soil and water conservation practices to prevent P loss in erosion, runoff, and leaching. Two reasons are usually given to justify the need for this upper critical limit. First is that a growing body of research shows that soils that are overfertilized with P relative to crop requirements will create an increased risk of nonpoint-source pollution of surface waters. Second is the concern that continuing to apply P to soils well beyond values that are needed for crop production contradicts the principles of ecological health and sustainable agriculture. The rationale underlying this second concern is the fact that P is obtained from a finite natural resource base, at a cost to society, and that agricultural practices that waste this resource are inconsistent with sustainability. Despite these concerns, there has been a reluctance to establish upper critical limits for soil test P presumably because (1) agronomic soil tests were not designed or calibrated for environmental purposes and (2) there may be an unjustified reliance on soil test P alone by environmental regulatory agencies attempting to control nonpoint-source pollution of surface waters, ignoring the complex interaction between soil P and the transport processes that move P from soil to water (see Chapters 6 and 8 for more information).

Other approaches to environmental soil testing for P are direct measurement of soluble or biologically available P, estimating potentially desorbable P by Fe oxide strips, and characterizing the degree of P saturation of soils. While research has been promising, to date none of these approaches has received widespread acceptance as a means to quantify the environmental risk associated with high-P soils. Readers are referred to the Supplementary Materials section of this chapter for more detailed information on this topic.

4.2.5 Limitations of Soil Testing

Soil testing is a valuable tool in any land-use program. Soil testing is not, however, a crystal ball, nor is it capable of providing absolute answers to all soil management questions. Some factors that affect the successful use of recommendations based on soil tests include the following:

- A soil test is only as good as the soil sample provided to the laboratory. A poorly collected sample can result in a recommendation that is completely inaccurate or inappropriate for the desired use of that soil. Carefully collecting a representative soil sample is essential.
- Because soil testing methods can definitely influence the analytical results obtained and the resultant recommendations, it is important to use the methods developed for your state or region.

Submitting samples to a laboratory that uses methods unsuitable for local soils can lead to inaccurate recommendations.

- Unexpected occurrences related to climate, management, or other uncontrollable factors can require adjustments in soil test recommendations. Most soil test recommendations are based on multiyear, multisite research with soils, plants, and climatic conditions typical to the region. Occasionally, however, conditions during a particular growing season may significantly affect the way that plants respond to soils and soil amendments. Plants may exhibit nutrient deficiency symptoms early in the year, but not later as soils warm and roots penetrate into subsoils. Insect or disease pressures or drought conditions can reduce yields and thus nutrient requirements. The use of in-season soil tests or plant analyses can help users of soil testing make needed adjustments in a soil test recommendation.

4.3 ENVIRONMENTAL TESTING PRACTICES FOR WATERS

One of the major goals of environmentally sound soil management practices is the protection of water quality. Preventing nutrients, organics (synthetic and natural), pathogens, sediments, and other pollutants from entering our surface waters or groundwaters is a national priority. Because of this, legislative mandates involving national standards have been established for the concentrations of many pollutants in surface waters and groundwaters. Waters that exceed these concentrations are considered impaired and in need of some form of corrective action to make them safe as drinking waters or to ensure that they are fishable and swimmable. Consequently, accurate water analysis methods are essential in efforts to prevent or reverse water pollution. Information related to the remediation of contaminated waters is discussed further in Chapter 12.

Water samples collected to monitor water quality are typically analyzed for organic and inorganic chemical composition, physical properties, and biological organisms according to well-established protocols for sampling, storage, and analysis. It is beyond the scope of this chapter to describe all aspects of water analysis in detail. However, an overview of key principles is provided below and references that give detailed information on the standard approaches to collect and analyze water samples are found at the end of the chapter.

4.3.1 Collection, Storage, Handling, and Analysis of Water Samples

Groundwaters, surface waters (fresh, estuarine, and saline), and wastewaters from municipalities and industries are the most common types of waters regularly analyzed in water quality monitoring programs. The parameters determined in a water analysis depend on the goal of the analysis. For example, if the goal is to determine if water is safe for human or animal consumption, the most common tests are for nitrate-nitrogen ($\text{NO}_3\text{-N}$), trace metals, pathogens, and organic chemicals. If the objective is to determine the potential impact of wastewater discharged from a point source on an aquatic ecosystem, analyses may include nutrients, biological oxygen demand (BOD), metals, and alkalinity. If surface waters are being tested to determine if they are eutrophic, they may be analyzed chemically for nutrients (N and P), oxygen (O_2), chlorophyll (a measure of algal productivity), and pH; physically for turbidity or depth of light penetration using a Secchi disk; and biologically for the rate of phytoplankton production. If the water or wastewater is being tested to determine its suitability for irrigation, analyses may include pH, alkalinity, salinity, and specific ions that are known to cause soil and plant problems, e.g., Na, Se, boron (B). A summary of the most common analyses conducted when testing groundwaters, surface waters, or wastewaters is provided in Table 4.1. Many other analyses can be conducted on waters, ranging from tests for hardness, aluminum (Al), chloride (Cl), and radioactivity to tests of the toxicity of the water to aquatic biota (e.g., fish, insects, mollusks, crustaceans). Readers are referred to *Standard Methods for the Examination of Water and Waste Water* (Clescerl et al., 1999) for a thorough description of water testing methods.

Table 4.1 Some of the More Common Parameters Measured in Groundwaters, Surface Waters, and Wastewaters

Physical	Inorganic Constituents	Organic Constituents	Microbiological
Color	Metallic elements:	Methane	Coliforms
Conductivity	Al, Ag, As, Ca, Cd, Cr, Cu,	Oil and grease	Fecal streptococcus
Odor	Fe, Mg, Mn, Na, Ni, Pb, Se,	Organic and volatile acids	<i>Campylobacter jejuni</i>
Oxygen transfer	Sr, Zn	Organic C	<i>Salmonella</i>
Solids		BOD	<i>Shigella</i>
Salinity	Nonmetallic constituents:	Chemical Oxygen Demand (COD)	<i>Legionella</i>
Taste	acidity, alkalinity, B, CO ₂ , Cl,	Pesticides	Enteric viruses
Temperature	F, I, NH ₄ , NO ₂ , NO ₃ ,	Phenols	Fe and S bacteria
Turbidity	dissolved O ₂ , pH, P, Si, SO ₄	Surfactants	Fungi, actinomycetes

As with any form of analysis, collection of a representative water sample is the first step in an effective water quality monitoring program. An important consideration for the collection of any type of water sample is the recognition that water composition is not constant within a water body. For example, vertical stratification can occur in lakes and reservoirs, flowing waters constantly alter water composition in rivers and streams, tidal influences can change the concentration of pollutants in estuaries, and seasonal variations induce temperature changes in the water column. Therefore, water sampling protocols must carefully consider both spatial and temporal variability to ensure that the goals of the monitoring program are achieved.

4.3.1.1 Surface Waters

When sampling surface waters it is important to consider sample location, sampling depth, and sampling frequency. If the impact of a point source on water quality is being monitored, samples should be taken at various points downstream from the point of discharge at measured time intervals after the influx of the pollutant. It is also important to sample different depths in the water body because variations in density and solubility can cause some pollutants to mix more thoroughly with waters than others. If nonpoint-source pollution is the major concern, a fixed sampling station near the outlet of a watershed is often used to monitor water quality continuously. In both situations there is a need to sample across the width and throughout the depth of the water body. In lakes and reservoirs where the residence time of the water is longer than in flowing waters, and where temperature differences with depth can be significant, sampling by depth and season is particularly critical to understand when and where pollutants are most likely to cause water quality problems. In flowing waters there is a need to sample at several points across the width of the river or stream because flow rates and water depths generally decrease near shore. Measuring flow velocity, as well as chemical composition, is a necessary step if the goal is to determine the mass (load) of pollutant emitted from a watershed to a water body.

The collection of surface runoff also demands special attention to determine the origin of the runoff accurately. A *watershed* is an area of land that drains its surface runoff to a specific point, often a river or other body of water. Obviously, the water in a river partially comprises surface runoff, but the river also contains contributions from groundwater sources and is influenced by in-stream processes such as settling of coarse particles and streambed erosion. A sample of water from the river, therefore, tells us little about the characteristics of surface runoff. To assess the characteristics of surface runoff accurately, it is important to collect samples of the water before it reaches the receiving body of water. It is also imperative that the area of land that is contributing water to the collection point be known. Surface runoff from natural watersheds can be collected

provided there is a single point of discharge. Alternatively, small watersheds (i.e., 1 to 10,000 m²) can be created by constructing barriers to prevent surface runoff from outside the area of interest and to direct surface runoff of interest to a common collection point.

4.3.1.2 Groundwaters

Groundwater sampling programs should consider most of the points mentioned above for surface waters. The main difference is that groundwater samples are collected from wells used for irrigation, drinking water, coal-bed methane, monitoring, etc. that are drilled to different depths in underground aquifers. Wells must be installed according to established protocols for accurate results, and groundwater samples must be handled very carefully to prevent changes that can occur when subsurface water is exposed to the atmosphere. It is also necessary to purge sampling wells prior to collection of the actual sample to be measured by pumping and discarding known volumes of water. This is because water that collects in the wells may differ in composition compared with water in the aquifer because in the well it has been exposed to different temperatures and atmospheric conditions. As with surface water samples, depth and spatial distribution of groundwater sampling points are important to determine accurately the extent of pollution of an aquifer and the direction of pollutant movement. In many cases groundwater sampling wells are “nested” at different depths and located at multiple points in transects along the path of groundwater movement.

Both remediation and prevention of groundwater contamination by nutrients, salts, heavy metals, trace elements, organic chemicals (natural and synthetic), pathogens and other contaminants require the evaluation of the composition and concentration of these constituents either *in situ* or in groundwater samples. Monitoring may require the analysis of physical properties, inorganic and organic chemical compositions, or microorganisms according to well-established protocols for sampling, storage and analysis. For example, if groundwaters will be used for human or animal consumption, the most appropriate tests would be NO₃-N, trace metals, pathogens, and organic chemicals. Several common constituents measured in groundwaters are listed in Table 4.1; however, other tests can be conducted on waters including tests for hardness, chlorine, radioactivity, or water toxicity.

Recommendations based on interpretation of the groundwater test results should be related to the ultimate use of the water. The interpretation and recommendation processes may be as simple as determining that a drinking water well exceeds the established maximum contaminant levels (MCLs) for NO₃-N and recommending the well should not be used as a drinking water source or that a purification system be installed (Table 4.2). However, interpretations of most groundwater analyses can be quite complicated and require additional information for proper interpretation. If a contaminant exceeds an acceptable concentration, all potential sources contributing to the pollution and pathways by which the contaminant moves must be determined. In many cases, multiple groundwater contaminants are present at different concentrations. Because the interpretation of water analyses is a complex process, recommendations should be based on a complete evaluation of the water's physical, chemical, and biological properties. Integrating water analyses into predictive models that can assess the effects of land use on water quality is needed in the long term to determine the most effective means to preserve and restore water quality.

Water samples are also subject to a number of changes after sampling that can alter their physical, chemical, and biological properties. Standard techniques for the proper storage and handling of water samples have been developed to ensure that analyses are not biased by changes in factors such as pH, oxidation–reduction status, or temperature after collection and prior to analysis. For example, samples to be analyzed for cations (e.g., Ca²⁺, Cu²⁺, K⁺, Mg²⁺, Na⁺, Ni²⁺, Pb²⁺, Zn²⁺) should be placed in a high-density polyethylene (HDPE) plastic bottle and acidified to a pH of <2.0 using nitric or sulfuric acid. This is done to prevent adsorption of the cations to the storage container and to minimize the precipitation of cations as insoluble carbonates or hydroxides during storage. Water samples that will be analyzed for anions (e.g., NO₃⁻, Cl⁻, F⁻, SO₄²⁻, PO₄³⁻) should be stored in HDPE bottles and refrigerated at temperatures <4°C. Organic chemicals

Table 4.2 Examples of MCLs for Drinking Waters

Contaminant	MCL^a (mg/L)	MCLG^b (mg/L)
<i>Inorganics</i>		
Arsenic (As)	0.006	0.006
Cadmium (Cd)	0.005	0.005
Chlorine (Cl)	4	4
Chromium (total Cr)	0.1	0.1
Copper (at tap Cu)	TT ^c	1.3
Cyanide (CN)	0.2	0.2
Fluoride (F)	4	4
Lead (Pb)	0.015	0
Mercury (inorganic Hg)	0.002	0.002
Nickel (Ni)	0.1	0.1
Nitrate (as N)	10	10
Selenium (Se)	0.05	0.05
Sulfate (SO ₄ ²⁻)	500	500
Thallium (Tl)	0.002	0.0005
<i>Radionuclides</i>		
Radon (Rn)	300 pCi/L	0
Uranium (U)	20 µg/L	0
<i>Organics</i>		
Alachlor	0.002	0
Atrazine	0.003	0.003
Benzene	0.005	0
Carbofuran	0.04	0.04
Carbon tetrachloride	0.005	0
Chlordane	0.002	0
2,4-D	0.07	0.07
Dinoseb	0.007	0.007
Dioxin	10 ⁻⁸	0
Endrin	0.002	0.002
Ethylene dibromide	0.00005	0
Heptachlor	0.0004	0
Lindane	0.0002	0.0002
Methoxychlor	0.04	0.04
Pentachlorophenol	0.001	0
Polychlorinated biphenyls (PCBs)	0.0005	0
Tetrachloroethylene	0.005	0
Toluene	1	1

(continued)

Table 4.2 Examples of MCLs for Drinking Waters (continued)

Contaminant	MCL ^a (mg/L)	MCLG ^b (mg/L)
Trichloroethylene	0.005	0
Vinyl chloride	0.002	0
Xylenes	10	10
Microbiological^d		
<i>Giardia lamblia</i>	TT	0
<i>Legionella</i>	TT	0
Total coliforms	TT	0
Viruses	TT	0

^a MCL = maximum contaminant level. Maximum permissible level of a contaminant in water which is delivered to any user of a public water system.

^b MCLG = maximum contaminant level goal. A nonenforceable concentration of a drinking water contaminant that is protective of adverse human health effects and allows an adequate margin of safety.

^c TT = treatment technique. Lowest value that can be achieved using best available technology.

^d TT — If a public water system is required to collect >40 samples/month, <5% of these can test positive for total coliforms. For *Giardia* and viruses, 99.9% removal/inactivation is expected.

Source: <http://www.epa.gov/safewater/mcl.html>.

(e.g., pesticides, nonvolatile hydrocarbons) are normally stored in amber glass bottles at <4°C to prevent photo-oxidation and microbial decomposition. Reducing agents are often added to these samples to prevent oxidation of the organic compounds during storage. Even if preserved properly, water samples cannot be stored indefinitely. Volatile or highly degradable substances in waters, such as O₂, NO₃⁻, PO₄³⁻, cyanide (CN⁻), should be analyzed quickly (<48 h). Water samples to be tested for pesticides and other organic chemicals should not be stored for more than 7 days; however, metals can be analyzed as much as 6 months after sampling if properly acidified and appropriate storage practices are followed.

A substance in a water sample may be present both in a dissolved state as well as adsorbed to sediment particles in the water. Phosphorus, for example, may be present in the water as dissolved P or as sediment-bound P (sometimes called particulate P). In a standard water analysis, the sample is filtered through a 0.45-μm filter. Anything that passes through the filter is considered to be in the dissolved state while that retained on the filter is described as sediment bound. Sediment-bound P is determined by the difference in total P concentration of the unfiltered sample and the P concentration in the filtered sample.

Example Problem 4.2

An analyst wishes to know the sediment, dissolved P, sediment-bound P, and total P concentrations in a water sample representing surface runoff from a small watershed. First, 100 mL of the sample is filtered through a 0.45-μm filter. The filter is dried and the amount of sediment retained on the filter is 20 mg. A 5-mL aliquot of the filtered water is diluted to 25 mL and this solution is found to have 0.2 mg P/L. A 10-mL sample is digested in strong acids and brought to 50 mL, and this digest solution is found to have 1.8 mg P/L.

Sediment concentration:

$$\frac{20 \text{ mg sediment}}{0.1 \text{ L water}} = \frac{200 \text{ mg sediment}}{\text{L water}}$$

Dissolved P concentration:

$$\frac{25 \text{ mL diluted water}}{5 \text{ mL original water}} \times \frac{0.2 \text{ mg P}}{\text{L}} = \frac{1.0 \text{ mg dissolved P}}{\text{L}}$$

Total P concentration:

$$\frac{50 \text{ mL digest}}{10 \text{ mL water}} \times \frac{1.8 \text{ mg P}}{\text{L}} = \frac{9.0 \text{ mg total P}}{\text{L}}$$

Sediment-bound P concentration:

$$\left[\frac{9.0 \text{ mg total P}}{\text{L}} \right] - \left[\frac{1.0 \text{ mg dissolved P}}{\text{L}} \right] = \frac{8.0 \text{ mg sediment-bound P}}{\text{L}}$$

Chemical, physical, and biological analyses of water samples must follow strict, well-defined protocols. A variety of methods are available to determine concentrations of inorganic, organic, and biological constituents in waters accurately and reproducibly. Detailed information on the proper means to handle and analyze water samples is available in several publications given in the references section at the end of this chapter.

4.3.2 Interpretation of Water Analysis Results

Interpretation is the process by which data obtained in a water analysis are used to develop recommendations on the suitability of the water for the desired end use. In some cases the interpretation process is simple and straightforward. For example, if a water analysis of a private drinking water well shows that it exceeds the established MCLs for a pollutant (e.g., $\text{NO}_3\text{-N}$), the recommendation would be to stop using the well as a drinking water source or to install purification technologies that can remove the pollutant from the water (see Table 4.2). Similarly, if wastewater discharged from a point source exceeds the regulatory criteria for BOD and nutrients, the recommendation would be to cease discharging the wastewater until steps have been taken to reduce these pollutants to acceptable levels.

In most cases, however, interpretations of water analyses can be quite complicated and require additional information for proper interpretation, which is particularly true for nonpoint-source pollution. If a lake, river, estuary, or aquifer exceeds the desired concentrations of a pollutant and no obvious point source exists, the interpretation process is very complex. Efforts must be taken to characterize all potential nonpoint sources that contribute the pollutant to the water body, the pathways by which the pollutant moves from land to the water, any channel processes that can affect the concentration of the pollutant, and the potential for bottom sediments in the water body to act as an ongoing or intermittent source (or sink) of the pollutant. It is not enough to measure the concentration of the pollutant in the water and determine if it exceeds standards established to protect public health or ecosystem stability. Society expects those involved in water pollution control to go farther and identify the causes of the pollution and the measures that can be taken to reduce the impacts of the pollutants on water quality. Further complicating the interpretation process is the fact that it is rare to find that only one pollutant is having an impact on water quality. In most cases, multiple pollutants are entering groundwaters and surface waters in different quantities, at variable rates, and from several locations in the watershed.

Interactions between pollutants are also common. For example, while N and P both contribute to *eutrophication*, the ratio of N:P is more important than the actual concentration of either nutrient (see Chapter 6). Similarly, we cannot accurately assess the extent of water quality degradation by measuring only one pollutant or by evaluating pollutant concentrations separately. This was illustrated in Table 2.4, which showed that several criteria (dissolved O₂, nutrients, light penetration, biomass, etc.) must be considered together to determine the extent of surface water eutrophication. Research has also shown that mixtures of metals and surfactants can be more toxic to fish than metals alone because the surfactants reduce the surface tension on gill membranes, increasing the permeability of the gill to the metals.

A good example of current efforts to interpret water quality analyses is the *National Water Quality Assessment Program* (NAWQA) conducted by the U.S. Geological Survey (USGS). The NAWQA program began in 1991 when the U.S. Congress charged USGS “to work with other federal, state, and local agencies to understand the spatial extent of water quality, how water quality changes with time, and how human activities and natural factors affect water quality across the Nation” (U.S. Geological Survey, 1999). The NAWQA program is assessing water quality in more than 50 major river basins and aquifer systems in the United States that affect >60% of the population in watersheds that cover about 50% of the total United States land area. Some preliminary results of this assessment are as follows:

- Streams and groundwater in basins with significant agricultural or urban development, or mixed land uses, almost always contain complex mixtures of nutrients and pesticides.
- Concentrations of N and P commonly exceed levels that can contribute to excessive plant growth in streams.
- Nitrate generally does not pose a health risk for residents whose drinking water comes from streams or aquifers buried relatively deep beneath the land. Health risks increase in those aquifers located in geologic settings that enable rapid movement of water. This finding raises potential concerns for human health, particularly in rural areas where shallow groundwater is used for domestic water supply (see Environmental Quality Issues/Events in Chapter 5).
- At least one pesticide was found in almost every water and fish sample collected from streams and in more than one half of shallow wells sampled in agricultural and urban areas. Concentrations of individual pesticides in samples from wells and as annual averages in streams were almost always lower than EPA drinking water standards. Effects of pesticides on aquatic life are a concern based on U.S. and Canadian guidelines.

As illustrated by the USGS NAWQA study, interpretation of water analyses results is a complex, somewhat daunting process, but one that is essential to the safe and efficient use of groundwaters, surface waters, and wastewaters. The most effective recommendations will be those that are based on multidisciplinary evaluations of the chemical, physical, and biological properties of waters. Integrating water analyses into predictive models that can assess the effects of land management on water quality is needed in the long term to determine the most effective means to preserve and restore water quality.

4.4 PLANT AND ORGANIC BY-PRODUCT ANALYSIS

In addition to soil and water testing, several other diagnostic procedures can improve the efficiency of land-use and management programs. The two most common practices are plant analysis and organic by-product analysis. Some of the key factors to consider when using plant and organic by-product tests are summarized below.

4.4.1 Principles of Plant Analysis

Plant analysis is defined as “the determination of the elemental composition of plants or a portion of the plant for elements essential for growth. It can also include determining elements that are detrimental to growth of animals or humans through our food chain” (Munson and Nelson, 1990). Accurate interpretation of the results of a plant analysis requires that calibration data exist that relate nutrient or nonessential concentrations in the plant to uptake of the element from the soil and/or growth response to additions of the element. The most common elements determined in a routine plant analysis are the essential plant nutrients: N, P, K, Ca, Mg, sulfur (S), B, chlorine (Cl), Cu, Fe, Mn, Mo, and Zn. In most cases, plant analysis results are compared to optimum nutrient ranges, with analytical values expressed in percentages (for major nutrients) and parts per million (ppm) or mg/kg (for micronutrients and nonessential trace elements), on a dry weight basis. Optimum nutrient ranges for many plants, especially agronomic plants, have been established by years of research and are found in many publications (see the Supplementary Materials section).

Example Problem 4.3

A 0.5-g sample of ground plant tissue is digested in a nitric/perchloric acid mixture and brought to 25 mL. The digest solution has 0.12 mg Cu/L. What is the Cu concentration in the original plant tissue?

$$\frac{0.025 \text{ L digest solution}}{0.0005 \text{ kg plant tissue}} \times \frac{0.12 \text{ mg Cu}}{\text{L digest solution}} = \frac{6.0 \text{ mg Cu}}{\text{kg plant tissue}}$$

As with soil and water testing, the collection, handling, and analysis of a plant sample must be done properly for useful results to be obtained. The main factors to consider when initiating a plant analysis program are summarized in Table 4.3. Specific guidelines for collecting samples for plant analysis including the plant part and number of plants to sample, the appropriate plant growth stage to collect, and any specific handling requirements for the sample can be obtained from the laboratory that will perform the analysis.

Plant analysis is most frequently used to confirm suspected deficiency situations and determine appropriate corrective applications (e.g., fertilization). However, research has also shown that plant analysis techniques have potential as monitoring tools to track in-season plant N needs (much like the PSNT test) or as postharvest tools for evaluating the success of N management for the current growing season (see Chapters 5 and 8). The leaf chlorophyll meter, an instrument that measures the “greenness” of the leaf and hence plant N status, has shown promise for use in management systems for corn where fertigation is possible. Likewise, the stalk NO_3^- test, in which a 15-cm section of the lower portion of a corn stalk is analyzed at physiologic maturity for NO_3^- -N, has been shown to be a good indicator of optimal or over-application of N to corn.

4.4.2 Principles of Organic By-Product Analysis

The most common types of organic by-products analyzed are animal manures and municipal biosolids, composts, and wastewaters from processing plants. Animal manures and municipal biosolids are extremely variable in composition, and the handling and analytical procedures used during analysis can greatly affect the accuracy and interpretation of the results. It is therefore important to consider carefully the factors described in Table 4.4 to ensure that a representative sample is obtained and analyzed properly. A recent publication also summarizes many important aspects of sampling and analysis of manures (Peters, 2003).

Table 4.3 Typical Components of a Modern Plant Analysis Program

Component	Comments
Sample collection	Accurate interpretation of a plant sample can only be accomplished by analyzing the appropriate part of the plant, collected at the correct stage of growth. Soil testing and plant analysis laboratories provide detailed sampling information for most plants. If sampling information is not available, the rule of thumb when collecting a plant sample is to select upper, mature leaves. Avoid leaves damaged by insects or disease or contaminated with fertilizers, dusts, or sprays. If possible, provide samples from healthy and deficient plants for comparative purposes. Be sure that these samples were collected at the same time, from the same plant parts, or the comparison will not be valid. After collection samples should be decontaminated by gently washing with deionized water or, if severely contaminated, a dilute (~0.1%) detergent solution. If a detergent solution is used, it must be followed by a thorough rinsing with pure water. Because the essential element most affected by contamination from soil or dust is Fe, if this is the element believed to be deficient, extreme care must be taken to eliminate surface contamination prior to analysis.
Sample preparation	Once contaminants have been removed, plant samples should be dried quickly at about 65 to 80°C (150 to 175°F). If samples cannot be dried immediately, store them under refrigeration (2 to 5°C) to avoid molding or organic matter decomposition. Samples should be dried in paper, cotton, or plastic mesh bags that allow adequate air movement during drying. After the samples have been dried, it is necessary to grind them to reduce the particle size and homogenize the sample prior to analysis. This is usually accomplished with a stainless steel grinding mill equipped with a 20- or 40-mesh screen. Dried, ground plant samples can be stored for long periods in glass or plastic vials, preferably at cool temperatures.
Sample analysis	Elemental analysis of a plant sample requires that the organic fraction of the sample be destroyed, leaving the mineral nutrients (P, K, S, Ca, Mg, Mn, Cu, Zn, Fe, B, etc.) either in solution or in a form that is readily dissolved. Two techniques have been developed for organic matter destruction, <i>wet digestion</i> and <i>dry ashing</i> . In wet digestion, plant samples are dissolved in concentrated mixtures of acids (HNO ₃ , HClO ₄ , H ₂ SO ₄) at high temperatures. Wet digestion is generally preferred for all elements, particularly with samples where Al, Fe, Zn, and S are of interest. Wet digestion is not recommended for B analysis because of problems with loss of B during the digestion and contamination from borosilicate glassware, some chemical reagents and other sources. Dry ashing refers to high-temperature (500°C) oxidation of a plant sample in a muffle furnace or high-temperature oven. This destroys the organic matter by combustion and leaves the mineral elements in the residual "ash." After combustion the ash is dissolved in an acid solution. The solution is filtered to remove undissolved solids and is then ready for analysis. Dry ashing is suitable for most elements as long as oven temperatures are carefully monitored. Excessive temperatures can cause volatilization losses of K and other elements. Once in solution, a wide variety of instruments are capable of determining nutrient concentrations. The most commonly used are the <i>atomic absorption spectrophotometer</i> (AAS, individual element analysis) and the <i>inductively coupled plasma spectrometer</i> (ICP, capable of multielement analysis on one sample). For certain elements (N, P, K, S, Mg, B, Ca) automated colorimetric analysis is acceptable.

Source: Adapted from Sims and Gartley (1996).

Interpretation of the results of an organic by-product analysis is a complex process that must reflect the effects of the by-product treatment process, storage, handling, application, and soil/crop management on the availability of nutrients and nonessential elements. It is beyond the scope of this book to cover all the details involved in the interpretation and use of organic by-product analyses. In many cases, comprehensive, specific analyses of municipal and industrial organic by-products are required of the by-product generators (e.g., municipal water treatment plant) and/or by-product users by state or federal regulatory agencies prior to land application. In most cases,

Table 4.4 Factors to Consider in the Collection and Analysis of Organic By-Products

Component of Organic By-Product Testing Program	Comments
Sampling and handling	The heterogeneity in organic by-product composition, combined with changes in by-product properties that occur during storage, means that great care is needed to obtain a representative sample. In general, the by-product should be sampled as close to the time of application as possible to minimize any changes that might occur between the time of sampling and application. Multiple subsamples of the by-product should be obtained and mixed thoroughly in a clean, plastic bucket. A representative subsample is then removed, placed in a plastic container, and immediately delivered to the testing laboratory. Avoid storing the sample for prolonged periods prior to analysis. Samples should be collected annually or whenever a change in any factor that might alter by-product composition occurs.
Analysis and interpretation	Organic by-product analyses should include, at minimum, total N, ammonium-N, and total P, K, Ca, and Mg. Additional analyses that can be conducted less frequently include total S, B, Mn, Cu, and Zn. Special tests that may occasionally be required are pH, soluble salts and some trace elements such as As, Mo, and Se. Total elemental concentrations are not used directly to determine the amount of plant-available nutrients in organic by-product because only a portion of the total amount of a nutrient in an animal by-product will be available during a normal growing season. The application rates of organic by-product are usually based on the amount of plant-available N anticipated to be provided by the by-product. However, the rates of other nutrients added when a by-product is applied, particularly P, should be considered to avoid excessive accumulations or imbalances of nutrients in soils that could have negative effects on plant growth or environmental quality. For municipal biosolids land application is also regulated based on the concentrations and loading rates of several trace metals (see Chapters 9 and 12).

Source: Adapted from Sims and Gartley (1996).

land application of biosolids is based on applying the agronomically optimum rate of N for the crop to be grown. However, federal regulations also establish the maximum concentration of trace elements and polychlorinated biphenyls (PCBs) permitted in biosolids used in land application programs, as well as the maximum annual and cumulative loading rate of these elements (see Chapter 8). State regulations may be similar to the federal rules or more restrictive. Key aspects of interpretation of organic by-product analyses are provided in Table 4.4. Readers are referred to the Supplementary Materials section of this chapter for more information.

4.5 ENVIRONMENTAL TESTING PRACTICES FOR AIR AND ATMOSPHERIC DEPOSITION

Air contains a variety of gaseous and particulate constituents that are of interest in environmental science. *Particulate matter* can consist of mineral particles (e.g., soil, asbestos, silica, fly ash, etc.), soot (black carbonaceous residue of incomplete fuel combustion), organic debris (e.g., animal dander, pollen, mold spores, coal dust, etc.), or aerosols (tiny droplets of liquid). Aerosols can carry bacteria, viruses, or other infectious agents. Particulate matter is often designated as PM_{10} or $PM_{2.5}$, which implies particles less than 10 or 2.5 μm , respectively. Particles of this size can be drawn deep into lung tissue and are considered a human health hazard.

The sampling and analysis of air involve a relatively straightforward process. The method employed depends on the physical state of the constituent of interest (gas or solid), the sensitivity of the available analytical procedures, and the concentration of the constituent of interest. For some constituents, methods exist to determine the concentration in air directly without collecting a sample for laboratory analysis (direct or real-time field measurements). Others simply require that a gas sample be collected and taken to the laboratory for analysis. If a constituent is present at low

concentrations, a known volume of air is passed through a physical or chemical trap (e.g., dust or spores trapped on a filter, or ammonia trapped in acid). The mass of the constituent (determined in the analysis) is divided by the volume of air that passed through the trap to obtain the concentration (mass per unit volume). Data from traps can also be calibrated using chambers with known concentrations of gases of interest. This approach is followed for the activated charcoal traps commonly used for radon testing in homes. Using the assumption that the radon concentration in the home is relatively constant over short (2 to 7 days) periods of time, data obtained from the trap (radioactive decay measured in picocuries, pCi) are compared to that obtained when similar traps are exposed to known concentrations of radon (measured in pCi/L) for the same length of time. The use of calibration chambers eliminates the need to know the volume of air sampled by the activated charcoal and therefore simplifies the deployment of the sampling devices such that they can be easily used by homeowners.

Several challenges exist in sampling air. For indoor air, the concentration of a given constituent may increase or decrease with height because some constituents are lighter or heavier than air, respectively. Indoor air is generally mixed through ventilation, heating, and cooling. The mixing may provide dilution or enrichment with constituents of interest and can complicate data interpretation. We must follow consistent sampling protocols to ensure that results are comparable over time or with established air quality standards. The U.S. Occupational Safety and Health Administration (OSHA) defines more than 500 *permissible exposure limits* (PELs) for constituents in indoor air that can be used as a guide in interpreting air sampling results. Table 4.5 presents PELs for selected air constituents. These limits represent the maximum concentration for exposure over an

Table 4.5 U.S. Occupational Safety and Health Administration Permissible Exposure Limits for Indoor Air Constituents

Constituent	Permissible Exposure Limit ^a
Acetone	2400 ^b
Ammonia	35
Arsenic	0.01
Asbestos	0.1 ^c
Benzene	3.2
Cadmium	0.01 – 0.05
Carbon monoxide	55
Ethylbenzene	435
Lead	0.05
Ozone	0.2
Parathion	0.1
Phenol	19
Trichloroethylene	537
Toluene	750
Xylene	435

^a Maximum allowable concentration assuming exposure for 8 h. All units are mg/m³ except for asbestos, which is expressed in fibers/cm³.

^b Concentrations for most organics are given in ppmv but have been converted here to mg/m³ for the sake of comparison. To convert, use the following relationships: ppmv = molecular weight/ V_m , where V_m = volume of 1 mol of gas calculated with V_m (L) = 62.36 (temperature in Kelvin)/pressure in mm Hg at atmospheric pressure (760 mm Hg) and 25°C (298 K), V_m = 24.45 L.

^c Units for asbestos are fibers/cm³.

Table 4.6 U.S. EPA National Ambient Air Quality Standards

Constituent	Standard ^a (μg/m ³)	Averaging Times
Carbon monoxide	10000	8 h
	40000	1 h
Lead	1.5	Quarterly average
Nitrogen dioxide	100	Annual
Particulate matter (PM ₁₀)	50	Annual
	150	24 h
Particulate matter (PM _{2.5})	15	Annual
	65	24 h
Ozone	157	8 h
	235	1 h
Sulfur oxides	80	Annual
	365	24 h

^a See footnote b in Table 4.4 for conversion to ppmv.

8-h period and were designed as worker protection standards. Higher concentrations would be allowed for short-term exposures.

When sampling air outdoors, challenges similar to those found with indoor sampling also exist. Dilution or enrichment may occur through wind action. Precipitation generally removes airborne constituents and sunlight may catalyze reactions such that air composition can change over the course of a day. The U.S. EPA Office of Air Quality Planning and Standards has established national ambient air quality standards, which are outlined in Table 4.6, for six principal pollutants for outdoor air. Those listed are primary standards, which are designed to be protective of human health, particularly for sensitive populations such as those with asthma, elderly individuals, and children. These standards are most often applied in urban areas although fires and wind-blown dust may cause temporary air quality issues in rural areas.

Example Problem 4.4

An air sampler collects PM_{2.5} particles on a filter for 12 h. Then 1440 L of air (airflow is 2 L/min) is drawn through the filter and 0.072 mg of particles is collected. Does the air meet the 24-h ambient air quality standards for PM_{2.5} shown in Table 4.6?

$$0.072 \text{ mg} \times \frac{1000 \text{ } \mu\text{g}}{\text{mg}} \times \frac{2 \text{ 12-h periods}}{24 \text{ h}} = \frac{144 \text{ } \mu\text{g}}{24 \text{ h}}$$

$$1440 \text{ L} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = 1.44 \text{ m}^3$$

$$\frac{144 \text{ } \mu\text{g} / 24 \text{ h}}{1.44 \text{ m}^3} = \frac{100 \text{ } \mu\text{g}}{\text{m}^3 - 24 \text{ h}}$$

The air does not meet the standard.

One aspect of outdoor air sampling that is particularly challenging is the characterization and quantification of emissions from a diffuse source. Examples include ammonia emissions from open-air animal feeding operations (e.g., cattle feedlots), methane emissions from a landfill, or fugitive dust emissions from an area affected by nonferrous metal mining activities (see Figure 9.2). The mixing of air masses that are or are not affected by the source greatly complicates interpretation of data reporting the concentrations of various constituents in air samples. Complicated micrometeorological techniques can be used to overcome some of these difficulties.

The Toxic Release Inventory (TRI) program of the U.S. EPA is a system that makes information publicly available regarding the storage and release of 650 potentially toxic substances. The program accounts for releases of toxic substances as fugitive air emissions (diffuse sources), point-source air emissions, onsite disposal or other releases, and offsite disposal or other releases. Data are generally reported as pounds of emissions per year for each of the relevant toxic substances for a given site. Air emissions are often estimated based on standard emission factors (e.g., burning 1 ton of coal produces a certain amount of emissions) but air sampling is often employed to verify data. Monitoring of a point source (e.g., a smoke stack or vent pipe) is relatively straightforward if we know the contaminant concentrations and the airflow. Measurement of fugitive air emissions presents the challenges discussed in the previous paragraph. Fugitive emissions are often referred to as “edge of fence” measurements. Measurements taken at the boundaries of a facility represent what actually leaves the company property and provides potential exposure to nearby residents.

The TRI program was developed in response to several industrial accidents in which residents living near industrial sites were unaware of the toxic nature of substances utilized at a facility. This information is now publicly available. In its current form, the legislation also provides a mechanism for a rough sketch of pollutant inventories and releases across the nation (see <http://www.epa.gov/tri/>). For example, a press release dated 23 June 2004 provided the most recent toxic release inventory data as of this writing and indicated that toxic releases decreased by 15% in 2002 compared to 2001. Initially, this seems like a positive trend; however, the decrease is actually the result of a legal decision affecting the mining industry and when this is factored into the estimates toxic releases actually increased by 5%.

Atmospheric deposition is the process by which substances present in the atmosphere are deposited on land or water. This process occurs as either wet or dry deposition. *Wet deposition* occurs when precipitation forming in the atmosphere picks up various constituents from the air and carries them downward as the precipitation falls to Earth. *Dry deposition* is the particulate matter (dust) that slowly settles to the Earth when gravity is able to overcome the ability of wind currents to keep particulate matter suspended in the atmosphere. Sampling of wet deposition simply involves collecting precipitation and analyzing it for the constituents of interest. For dry deposition, collection pans of known size receive particulate matter for a specified period of time and are periodically washed down to consolidate the dry material and to facilitate analysis. The collection pans must be protected from precipitation so that wet and dry depositions are not co-mingled. Generally, the dry deposition measuring devices have a cover that moves over the collection pan when a sensor detects the beginning of a precipitation event.

There are several situations in which atmospheric deposition can have an environmental impact on land or water. *Acidic deposition* (see Chapter 11) causes significant impacts on structures, vegetation, and aquatic and terrestrial habitats. Acidic deposition is frequently called acid rain or acid precipitation but acidic deposition is more appropriate because it has substantial wet and dry components. *Nutrient enrichment* of surface waters via atmospheric deposition is another situation (see discussion of airsheds in Chapter 2) in which a significant ecological impact can occur from wet or dry deposition. Figure 4.2 shows isopleths for wet deposition of nitrate plus ammonium across the United States. The sources of the N include combustion of

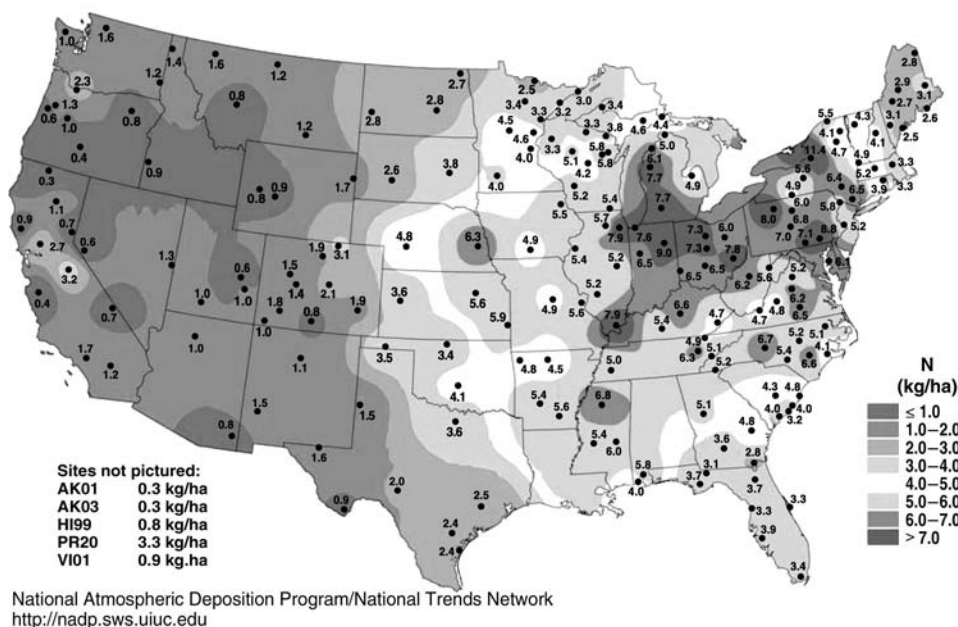


Figure 4.2 Inorganic nitrogen wet deposition from nitrate and ammonium in 2003 across the United States. (From National Atmospheric Deposition Program (NRSP-3)/National Trends Network. 2004. NADP Program Office, Illinois State Water Survey, Champaign, IL.)

fossil fuels, use of N fertilizers, and animal feeding operations. Wet deposition of N can be as high as 9 kg N/ha. This value can represent as much as 5 to 10% of the N applied to turf or to some crops, but is also only a small fraction of that applied for crops that are high users of N (e.g., corn at >200 kg N/ha). In the United States, atmospheric deposition of N and S compounds are decreasing with time because of emission control efforts.

PROBLEMS

- 4.1 Soil sample collection is one of the most critical aspects of the soil testing process. Explain how you would decide where to collect soil samples for (a) a corn–soybean rotation on a 100-ha dairy farm; (b) a mine spoil area that is to be revegetated and used as pastureland for beef cattle; (c) a Pb-contaminated soil that must be remediated prior to use as parkland.
- 4.2 Chemical soil test extractants remove “plant available” nutrients from soils by dissolution, desorption, and chelation. How would you make 10 L of the following soil test extractants:
 - a. Mehlich 1: 0.05 M HCl + 0.0125 M H₂SO₄?
 - b. Mehlich 3: 0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA?
 - c. Ammonium bicarbonate-DTPA: 1 M NH₄HCO₃ + 0.005 M DTPA?
- 4.3 Using Figure 4.1, discuss the concept of a soil test “critical value” — what it means and how its interpretation differs when crop yield is the main goal compared with protection of human health and environmental quality.
- 4.4 What impacts could urbanization have on the water quality of a river that flows through the development? How do cities prevent the contamination of their drinking water sources? Are water pollution problems always associated with human activities?
- 4.5 Explain the difference between a total maximum daily load (TMDL) and an MCL. What is the value of establishing TMDLs for use in watershed-scale water quality protection efforts?

- 4.6 Water quality monitoring programs must follow strict QA/QC protocols for sample collection, storage, and handling. Explain the justification for the time, effort, and expense needed to follow rigorous QA/QC protocols.
- 4.7 You are asked to determine if the water in a newly drilled well is safe for use as drinking water because of concerns in the region about $\text{NO}_3\text{-N}$ contamination of the aquifer. You collect a sample, bring it back to the laboratory, dilute it tenfold with deionized water, analyze it colorimetrically for $\text{NO}_3\text{-N}$, and obtain the following results, along with data from the standard curve you prepared using solutions of known $\text{NO}_3\text{-N}$ concentrations:

Concentration of $\text{NO}_3\text{-N}$ in Standard Solution, mg $\text{NO}_3\text{-N/L}$	Absorbance
0	0
0.25	0.042
0.5	0.080
1.0	0.159
2.0	0.308
5.0	0.803

- Absorbance of the diluted well water sample equals 0.094. Show how you would determine the concentration of $\text{NO}_3\text{-N}$ in the water sample graphically and also by use of a linear regression equation. Is the well water safe for use as a drinking water supply (compare your results with Table 4.2)?
- 4.8 Locate the USGS National Water Quality Assessment Program report “The Quality of Our Nation’s Waters: Nutrients and Pesticides” on the USGS home page on the Internet (<http://www.water.usgs.gov/pubs/circ/circ1225/>). Review the section entitled “Modeling Integrates Information to Assess Risks of Nitrate Contamination to Shallow Ground Water.” Explain the use and value of this modeling effort to the national effort to improve groundwater quality.
- 4.9 You digested a 0.5-g corn ear leaf sample in concentrated nitric-perchloric acid. The digested solution is filtered into a 50-mL volumetric flask and made to volume with deionized water. The concentration of P in the diluted solution is 30 mg P/L. What is the concentration of P in the corn ear leaf in mg/kg and percent?
- 4.10 Explain the difficulties likely to be encountered when interpreting an organic waste analysis and making a recommendation for the proper waste application rate.
- 4.11 Why is it important to develop a sampling program before beginning to collect field samples? What are some reasons for including a QA/QC program in the evaluation of contaminated site investigations?
- 4.12 When 200 L of air is passed through 500 mL of a sulfuric acid solution acting as a trap for ammonia, the sulfuric acid solution contains 3.0 mg $\text{NH}_4\text{-N/L}$. Does the air meet the personal exposure limits for ammonia outlined in Table 4.5?

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PART II

**Nutrients, Management, and
Environmental Quality**

Soil Nitrogen and Environmental Quality

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5.1 NITROGEN AND THE ENVIRONMENT

Nitrogen (N) is arguably the most important and yet most difficult to manage of all the plant nutrients. While absolutely vital to modern agriculture, it also has a number of serious environmental impacts, briefly summarized in Table 5.1. This chapter focuses on the forms and cycling of N in soils, emphasizing the issues of greatest importance to environmentally sound soil N management. We will address the following key questions:

- What is the basis for public concerns about the effects of N on human and animal health, its role in the pollution of groundwaters and surface waters, the formation of acid rain, and the destruction of the stratospheric ozone layer?
- What are the forms of N in soils that are of greatest importance to agriculture and other land uses? How well do we understand the physical, biological, and chemical processes that control transformations between the various organic and inorganic forms of soil N?

Table 5.1 Summary of Environmental Problems Associated with Nitrogen

Environmental Issue	Causative Mechanisms and Impacts
Human and Animal Health	
Methemoglobinemia	Consumption of high-nitrate drinking waters and food; particularly important for infants because it disrupts O ₂ transport system in blood
Cancer	Exposure to nitrosoamines formed from reaction of amines with nitrosating agents; skin cancer increased by greater exposure to ultraviolet radiation resulting from destruction of the O ₃ layer
Nitrate poisoning	Livestock ingestion of high-nitrate feed or water
Ecosystem Damage	
Groundwater contamination	Nitrate leaching from fertilizers, manures, sludges, wastewaters, septic systems; can impact both human and animal health, and trophic state of surface waters
Eutrophication of surface waters	Soluble or sediment-bound N from erosion, surface runoff, or groundwater discharge enters surface waters; direct discharge of N from municipal and industrial wastewater treatment plants into surface water; atmospheric deposition impacts water quality and biological diversity of fresh waters
Acid rain and ammonia evolution and redeposition	Nitric acid originating from reaction of N oxides with moisture in atmosphere is returned to terrestrial ecosystem as acidic rainfall, snow, mists, fogs (wet deposition) or as particulates (dry deposition); damages sensitive vegetation, acidifies surface waters, and, as with eutrophication, can unfavorably alter biodiversity in lakes, streams, bays; ammonia evolved from concentrated animal feeding operations can acidify soils and alter species diversity in nearby woodlands
Stratospheric ozone depletion and global climate change	Nitrous oxides from burning of fossil fuels by industry, automobiles, and from denitrification of nitrate in soils are transported to the stratosphere where O ₃ destruction occurs; ultraviolet radiation incident on earth's surface increases, as does global warming

Source: Adapted from Keeney (1982).

- What soil, environmental, and management factors control N availability to plants and the movement of N from land to air and water? How can we use our knowledge of the many complex chemical and biological processes in the *soil N cycle* to improve management of all N sources, from fertilizers to animal manures, municipal biosolids (e.g., sewage sludges), and industrial organics? [See Chapter 8, Nutrient Management Planning, for detailed discussions of best management practices (BMPs) for soil N and the organic and inorganic N sources used as soil amendments].

5.1.1 Origin and Distribution of Nitrogen in the Environment

To understand fully the environmental problems caused by N, and to develop sensible, cost-effective approaches to N management, it is essential to have a basic understanding of the origin and cycling of N in the Earth's four major "spheres": lithosphere, hydrosphere, atmosphere, and biosphere (see Chapters 2 and 3 for discussion of these spheres). Most (>98%) of the Earth's N is found in the lithosphere, either in the Earth's core, in igneous and sedimentary rocks, oceanic sediments, or soils. The remaining 2% is distributed between the atmosphere, hydrosphere, and biosphere. In the atmosphere, N exists mainly as the inert gas N₂, which comprises 78% of

atmospheric gases. In the hydrosphere, N occurs as dissolved organic or inorganic N. Nitrogen is also a vital component of the biosphere, which consists of living plants and animals. Nitrogen can be found in many different forms in these spheres, including molecular N, organic molecules, geologic materials, gases, and soluble ions.

Nitrogen is a very dynamic element, capable of being transformed biochemically or chemically through a series of processes conceptually summarized as the *nitrogen cycle* (Figure 5.1). Most N transformations involve the *oxidation* (loss of electrons) or *reduction* (gain in electrons) by the N atom from both biological and chemical processes. The oxidation states of N in nature range from +5 in the nitrate anion (NO_3^-) to -3 for ammonia (NH_3) or ammonium (NH_4^+). The soil N cycle (Figure 5.2 and Section 5.2) is a subset of the overall N cycle. We seek to understand how management of the soil N cycle affects other segments of the global N cycle, such as groundwater aquifers in the hydrosphere.

In the broadest sense, there are three major natural inputs to the soil N cycle: *atmospheric deposition*, *biological N fixation*, and *weathering and decomposition*. Atmospheric deposition occurs as inorganic and organic N in precipitation or dry particulate matter. Biological N fixation is the conversion of gaseous, atmospheric N_2 to NH_3 and then organic N by symbiotic and nonsymbiotic organisms. Weathering and decomposition reactions are those in which previously fixed or deposited organic or inorganic N is transformed from stable inorganic or organic N to more chemically and biologically active forms of N. The major natural processes by which N is lost from soils are by evolution as a gas (NH_3 volatilization and *bacterial or chemical denitrification* of NO_3^- to gaseous N oxides) and by transport processes as soluble N in waters percolating

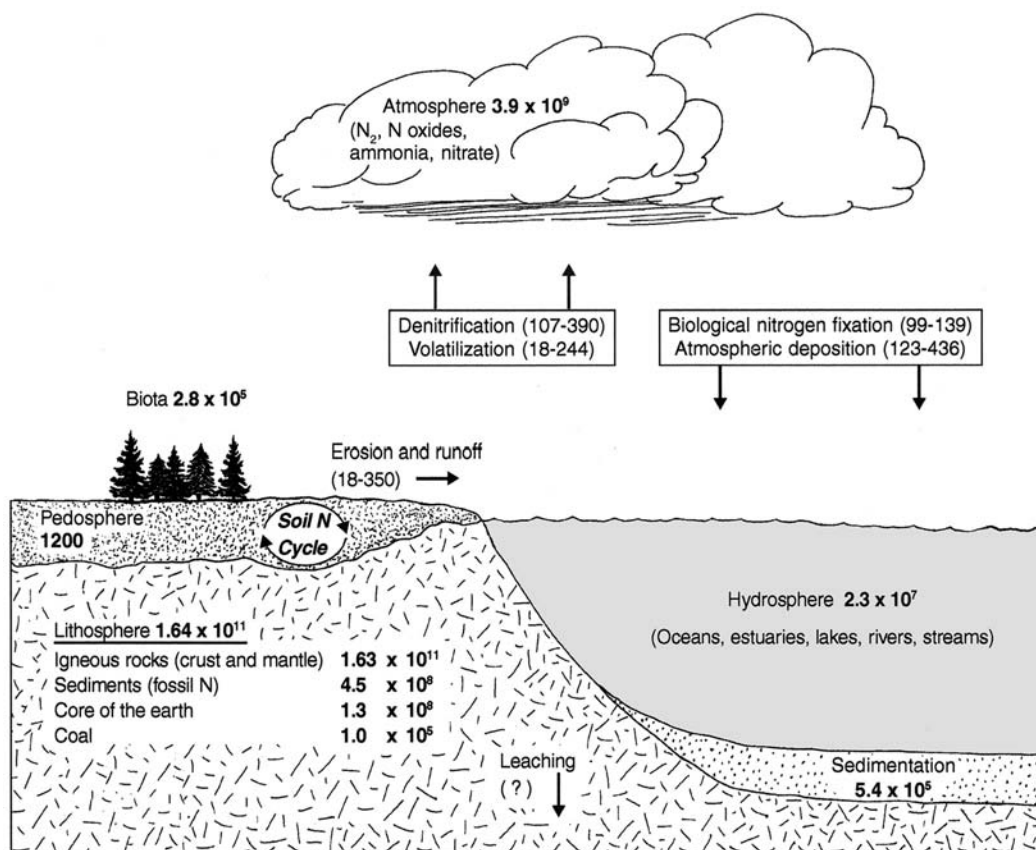


Figure 5.1 The global nitrogen cycle (units = Terrograms = Tg). Inset indicates soil N cycle, shown in more detail in Figure 5.2. (Data from Hauck and Tanji, 1982; Stevenson, 1982.)

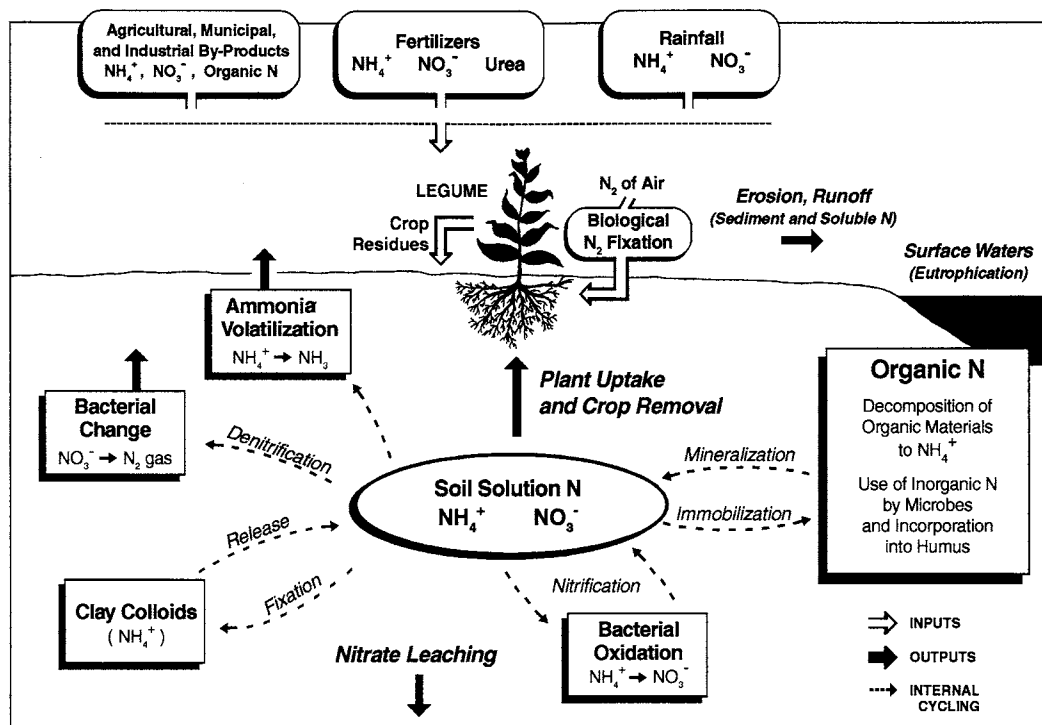


Figure 5.2 The soil nitrogen cycle.

downward through soils (*leaching*) or in water and sediments moving across the soil surface (*erosion* and *runoff*). Soil N management primarily involves manipulating or supplementing (e.g., fertilization, manuring) natural processes to produce plants for food, fiber, or aesthetic purposes. Environmental concerns about N arise when one of these transformations results in the conversion and concentration of N in a form that can adversely affect the health or quality of an organism or ecosystem. It is important to remember that, although only a few forms of N are now regarded as harmful to our environment, the processes of the N cycle regulate, on global and local scales, the amount of N in each form. Controlling pollution caused by N, therefore, starts with an understanding of how to control N cycling in soils and other ecosystems.

Global estimates of long-term changes in the distribution of N among the four spheres are filled with uncertainty. However, human activities have clearly influenced this distribution, enriching some sectors of the Earth's environment with N while simultaneously depleting others. Many fundamental aspects of modern civilization, such as agriculture, urbanization, industry, transportation, and water or waste treatment systems can significantly affect the distribution of N at local scales, and cumulatively, on a global scale. Unfortunately, human-induced movement of an element, such as N, to a part of the environment where it can have a negative effect is often a synonym for pollution. Although there can be a wide variety of environmental impacts from the redistribution of N, from the perspective of soil N management the forms of N of greatest importance are NO_3^- , NH_3 , and the nitrous oxides (N_2O , NO). Our understanding of the mechanisms by which NO_3^- leaching, NH_3 volatilization and re-deposition to soils and waters, and nitrous oxide emissions from soils to the atmosphere result in pollution is far from complete. However, we do have a basic understanding of these processes and have developed many practical means to minimize the effects of N on soil, air, and water quality.

5.1.2 Nitrogen Effects on Human and Animal Health

Nitrogen can have both beneficial and detrimental effects on human health. An adequate supply of N in human diets is essential for physiological health, body structure, immunological responses to disease, and cognitive performance. For good health, humans require a minimum of 2 kg N/year and the World Health Organization (WHO) recommends 0.75 g protein/kg bodyweight/day. Diets that are deficient in N can result in growth retardation in children, muscle wasting, fat accumulation in the liver, altered mental status and capacity, lethargy, fatigue, anemia, and increased susceptibility to disease (Wolfe and Patz, 2002). Managing soil N to produce food that provides adequate protein for human diets is one of agriculture's most important roles.

Deleterious effects of N on human health are most commonly due to overexposure to N oxides (NO_x) in the atmosphere and NO_3^- in drinking waters. Biologically, NO_x act as a strong oxidant that, upon inhalation, can damage lung cells and lead to increased potential for respiratory diseases and exacerbation of other health conditions such as asthma, particularly in young children. Episodes of severe air pollution have also been shown to be associated with higher hospital admissions for coronary problems. Despite growing concerns about NO_x and human health, there is little doubt that groundwater, and more specifically drinking water, contamination by NO_3^- remains the environmental issue of greatest concern for N management. For decades, the major human and animal health issues associated with the consumption of excessive NO_3^- in drinking waters, or even in some foods, has been *methemoglobinemia* ("blue-baby syndrome"). Methemoglobinemia is not caused directly by NO_3^- but occurs when NO_3^- is reduced to nitrite (NO_2^-) by bacteria found in the digestive tract of humans and animals. Nitrite can then oxidize iron (Fe) in the hemoglobin molecule from Fe^{2+} to Fe^{3+} , forming methemoglobin, which cannot perform the essential oxygen transport functions of hemoglobin. This can result in a bluish coloration of the skin in infants, hence the origin of the term "blue baby syndrome." Symptoms include nausea, vomiting, and dizziness. Methemoglobinemia is a much more serious problem for very young infants than adults because after the age of 3 to 6 months, the acidity in the human stomach suppresses the activity of the bacteria that transform NO_3^- to NO_2^- . Although documented cases of methemoglobinemia are rare, the U.S. Environmental Protection Agency (EPA) has established a maximum contaminant level of 10 mg NO_3^- -N/L (~45 mg NO_3^- /L) to protect the safety of U.S. drinking water supplies. Animals can also be susceptible to methemoglobinemia, although the health advisory level for livestock is much higher, ~40 mg NO_3^- -N/L (180 mg NO_3^- /L).

More recently, another major human health concern with NO_3^- in drinking waters has been the potential carcinogenic effect of N-nitroso compounds. These compounds are produced when NO_3^- is reduced to NO_2^- and nitrosation reactions generate organic compounds with the structure $\text{R}_2\text{N}-\text{N}=\text{O}$, where R is any carbon group. Elevated NO_3^- concentrations in drinking waters have been linked in some epidemiological studies with increased incidences of bladder, liver, ovarian, and stomach cancers. Finally, high NO_3^- inputs into freshwaters, estuaries, and coastal waters may contribute to eutrophication and increase the frequency of harmful algal blooms (HAB; Anderson et al., 2002). Neurotoxins and hepatoxins produced during HABs, sometimes referred to as "red tides," have been found to cause injury or death to livestock and wildlife, but documented cases of HAB effects on humans are very rare.

Example Problem 5.1

Evaluating results from different studies requires that we make sure that the units of expression for experimental data, or environmental standards, are comparable. For example, the drinking water standard used for nitrate in the United States is expressed in mg of nitrate-nitrogen per L (U.S. standard = 10 mg NO_3^- -N/L). In Europe, the standard is expressed as mg of nitrate molecule per L

(e.g., European standard = 50 mg NO₃⁻/L). Conversion of units shows that these two standards are essentially the same:

Atomic weights: N = 14 g and O = 16 g

Molecular weight of nitrate (NO₃⁻) = [14 + (3 × 16)] = 62 g/mol

% N in one molecule of NO₃ = [14 g ÷ 62 g] = 0.225 (22.5%)

Therefore, drinking water with a concentration of 50 mg NO₃⁻/L:

$$50 \frac{\text{mg NO}_3^-}{\text{L}} \times (0.225) = 11.3 \text{ mg NO}_3\text{-N/L}$$

Environmental Quality Issues/Events

The USGS National Water Quality Assessment Program (NAWQA)

In 1991, the U.S. Congress authorized the U.S. Geological Survey (USGS) to undertake a national assessment of water quality focusing on more than 50 major river basins and aquifer systems. These water resources cover about half the land area in the United States and affect more than 60% of the U.S. population. The overall goal of NAWQA was to help resource managers and policy makers to “better anticipate, prioritize, and manage water quality in different hydrologic and land-use settings and to consider key natural processes and human factors in resource strategies designed to restore and protect water quality” (USGS, 1999). The NAWQA program initially focused on the nutrients N and phosphorus (P) and the pesticides in groundwaters and surface waters; later efforts addressed radon, trace elements, and industrial chemicals. Results from the first 20 NAWQA study units (Figure 5.3a) were published by USGS in 1999 (The Quality of Our Nation’s Waters: Nutrients and Pesticides). Given the human health concerns mentioned above, a major focus of the initial studies was the relationship between land use, management practices, hydrologic and geochemical processes, and NO₃⁻ contamination of U.S. groundwaters. Key findings of the NAWQA study, with respect to groundwater NO₃⁻, were as follows:

Background concentrations are low: Background samples were collected from undeveloped areas minimally affected by agriculture, urbanization, and other human-impacted land uses. Background NO₃⁻ levels are mainly controlled by naturally occurring minerals and biological processes but can be altered by atmospheric deposition and changes in soil processes from inputs of rainwater contaminated by human activities (e.g., acid deposition). The national background concentration for NO₃⁻ in shallow groundwaters is 2 mg NO₃-N/L.

Human activities have increased groundwater NO₃⁻ above background concentrations, in some, but not all settings: In 53% of shallow groundwaters from agricultural and urban areas, median NO₃⁻ concentrations were above the national background. However, only 3 of the 33 major aquifers studied had median NO₃⁻ concentrations above background; all three were beneath agricultural areas (Figure 5.3b).

Nationally, the risk to human health from NO₃⁻-contaminated groundwaters is greatest for those drinking water from shallow aquifers: The highest percentage of groundwater samples exceeding the EPA drinking water standard (10 mg NO₃-N/L) was seen in shallow (<100 ft or 33 m) aquifers (Figure 5.3c). Values were lower in deeper aquifers because of mixing with uncontaminated deep aquifer waters and the protective effect of geological materials overlying deep aquifers.

High concentrations of NO₃⁻ in shallow groundwaters were widespread and strongly related to agricultural land use, but no regional patterns were apparent: Median NO₃⁻ concentrations for 13 of 36 agricultural aquifers were >5 mg NO₃-N/L. Only 1 of 13 urban areas was in the high NO₃⁻ concentration group (Figure 5.3d and e). The generally more widespread and intensive use of fertilizers and manures in

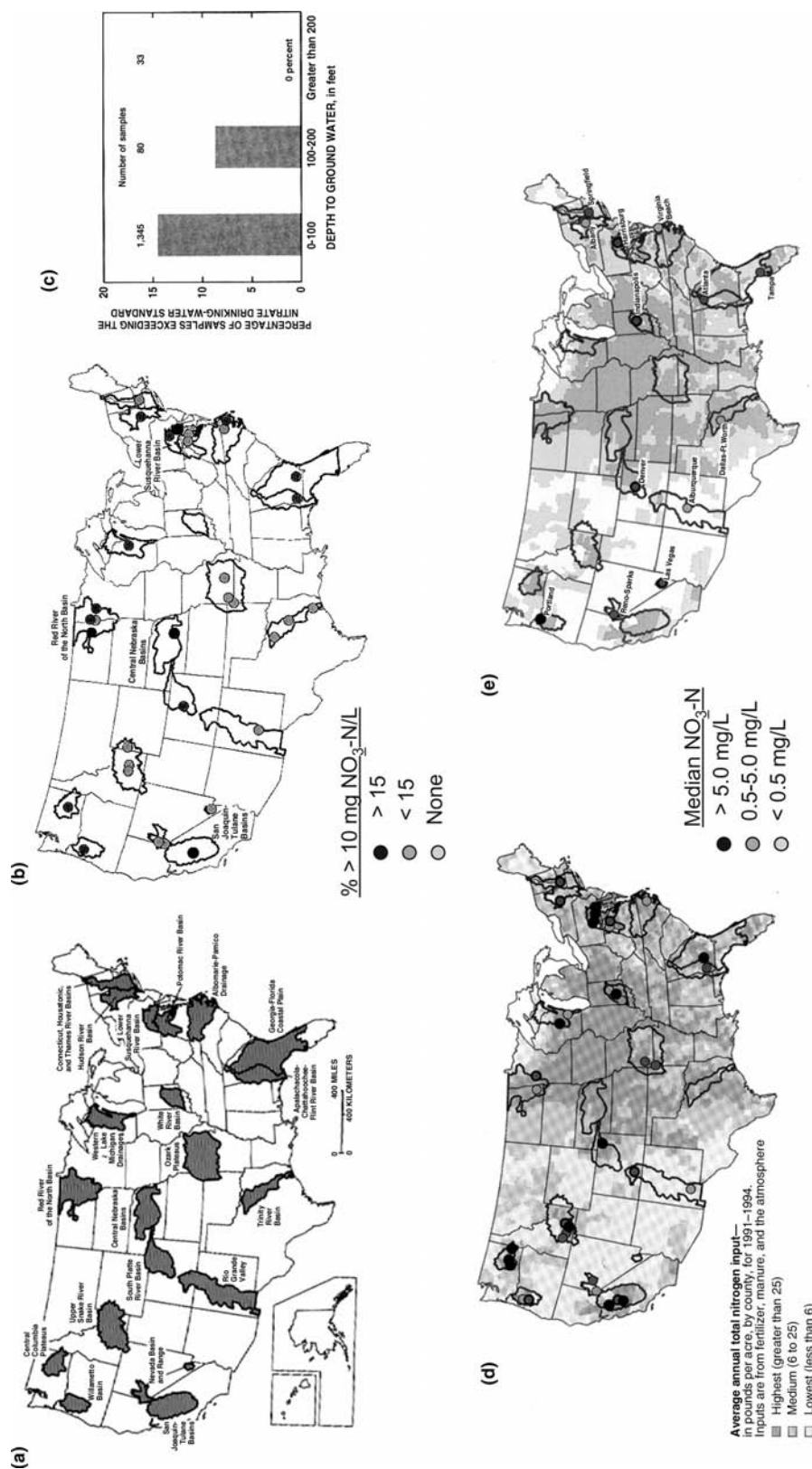


Figure 5.3 Trends from the USGS NAWQA. (a) First 20 study units of the NAWQA program; (b) national ranking of $\text{NO}_3\text{-N}$ concentrations in major aquifers; (c) percentage of groundwater samples exceeding the U.S. drinking water standard ($10 \text{ mg NO}_3\text{-N/L}$) is greatest for shallow groundwater aquifers ($<100 \text{ ft}$); (d) $\text{NO}_3\text{-N}$ concentrations in shallow groundwater aquifers from agricultural areas were among the highest measured, but did not always exceed the national background concentration ($2 \text{ mg NO}_3\text{-N/L}$); (e) Urban areas generally had lower $\text{NO}_3\text{-N}$ concentrations in shallow groundwater aquifers but about 40% of urban areas surveyed had median values above the national background concentration. (From USGS, 1999.)

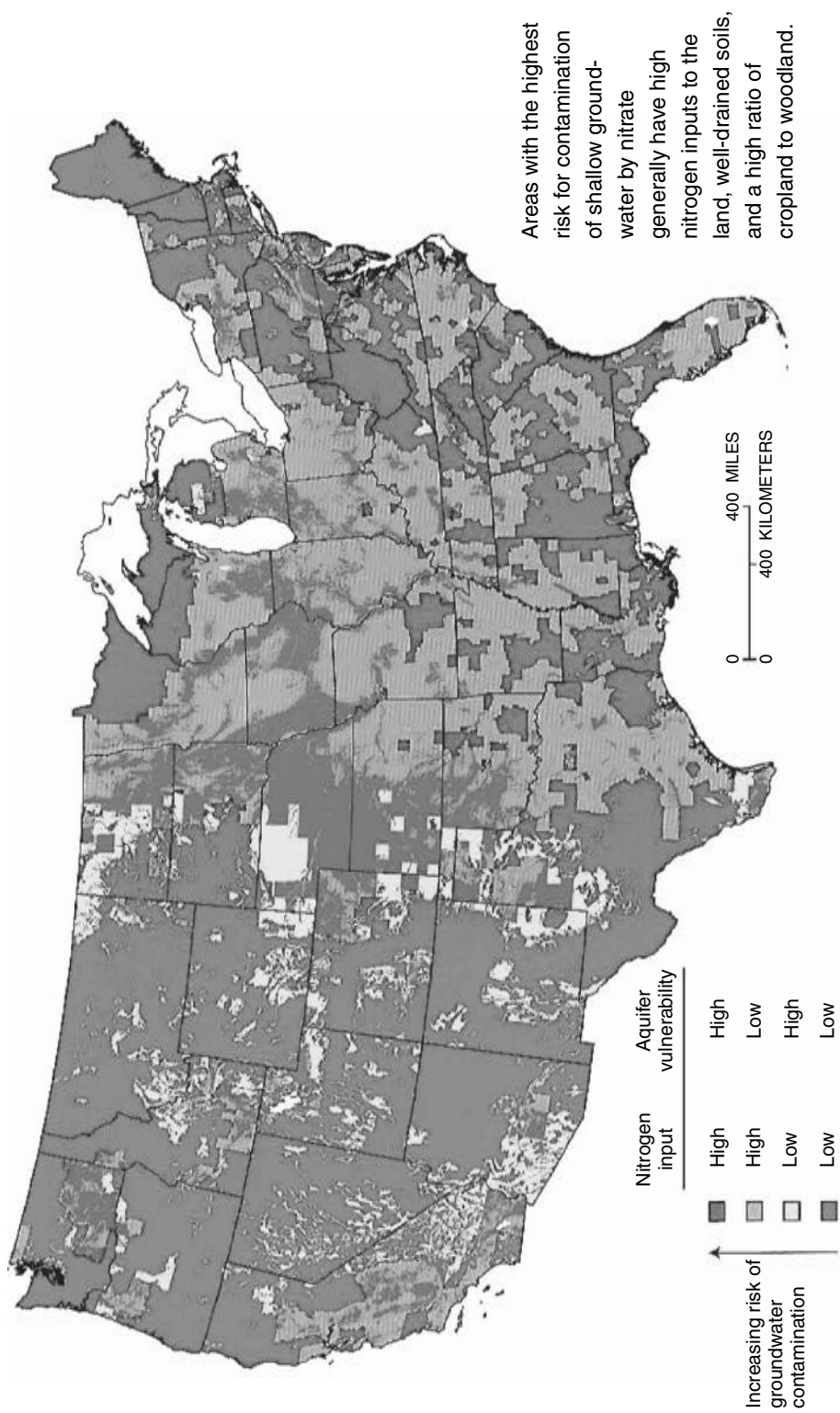


Figure 5.4 (Color figure follows p. 242.) Geographic nature of the estimated risk of $\text{NO}_3\text{-N}$ contamination of groundwater in the United States based on a USGS model integrating nitrogen inputs and aquifer vulnerability. (From USGS, 1999.)

agricultural areas and higher impervious surfaces in urban areas (more runoff, less infiltration to groundwaters) were cited as causative factors for these trends.

A USGS model was developed to estimate the risk of NO_3^- contamination of shallow groundwaters: The model integrates N inputs (fertilizers, manures, atmospheric inputs, population densities — to represent septic system inputs of N) and aquifer vulnerability (based on soil drainage characteristics, woodland vs. cropland density in watersheds) using Geographic Information Systems (GIS). The areas identified by this model as having the highest risk for NO_3^- contamination generally corresponded to monitoring results from the 20 NAWQA study units (compare model output in Figure 5.4 with Figure 5.3). Highest-risk areas have high N inputs, well-drained soils, and high ratios of cropland to woodland.

5.1.3 Nitrogen and Eutrophication

Eutrophication is defined as an increase in the nutrient status of natural waters that causes accelerated growth of algae or water plants, depletion of dissolved O_2 , increased turbidity, and a general degradation of water quality. Causes and management of eutrophication are discussed in more detail in Chapters 2 and 6, but enrichment of lakes, ponds, bays, and estuaries by N and P from surface runoff or groundwater discharge is known to be a contributing factor. Concentrations of total N (N_t) required to induce eutrophication in fresh and estuarine waters are much lower than the values associated with drinking water contamination. Although estimates vary, and depend considerably on the N:P ratio in the water, concentrations of 0.5 to 1.0 mg N_t/L are often used as threshold values for eutrophication. Marine environments, where salinity levels are greater, are more sensitive to eutrophication, and thus have lower threshold levels of N (<0.6 mg N_t/L). The EPA recently developed “eco-regional nutrient criteria” for N (and P; see Chapter 6), defined as “reference ecological conditions characteristic of a given geographical region.”* States may use these criteria to set legally enforceable nutrient standards for lakes, reservoirs, rivers, and streams in the future. Eco-regional criteria for N_t range from 0.12 to 2.18 mg N_t/L for rivers and streams and 0.10 to 1.27 mg N_t/L for lakes and reservoirs.

It is important to remember that N concentrations in surface waters reflect not only agricultural inputs (primarily nonpoint in nature), but the inputs of N from direct discharge of wastewaters from municipalities, industry, and recreational developments. Other sources of the total pool of N in surface waters are (1) atmospheric deposition, both in precipitation (e.g., “acid deposition” as HNO_3 and re-deposition of volatilized NH_3) and as particulate matter (e.g., dusts from wind erosion and particulates from industrial emissions) and (2) biological N fixation of atmospheric N_2 by aquatic organisms.

National analyses of the contributions of various land uses to total N discharge to surface waters have also been conducted in the NAWQA program and other studies. The goal has been to guide land use planning efforts designed to reduce eutrophication. For example, a comparison of total N entering surface waters from point-source discharge and from nonpoint sources via stream flow showed that agriculture is the major source of stream total N yield in many U.S. watersheds (Figure 5.5). Nonpoint N pollution of surface waters was also found to be much more significant than that originating from point sources. Another large-scale analysis of nonpoint N pollution was conducted for the Mississippi–Atchafalaya River Basin (MARB), which drains about 3.3 million km^2 (41%) of the United States, and is the largest river basin in North America and third largest in the world (Figure 5.6). The MARB contains some of the most productive farmland in the world (58% of the basin is cropped) and has a population of about 70 million people. Most of the corn, soybeans, cattle, and pigs produced in the United States are grown in the MARB area. The driving force for this study was growing concern about *hypoxia* (dissolved O_2 levels < 2 mg/L) in the Gulf

* Refer to <http://www.epa.gov/waterscience/standards/nutrient.html> for eco-regional nutrient criteria.

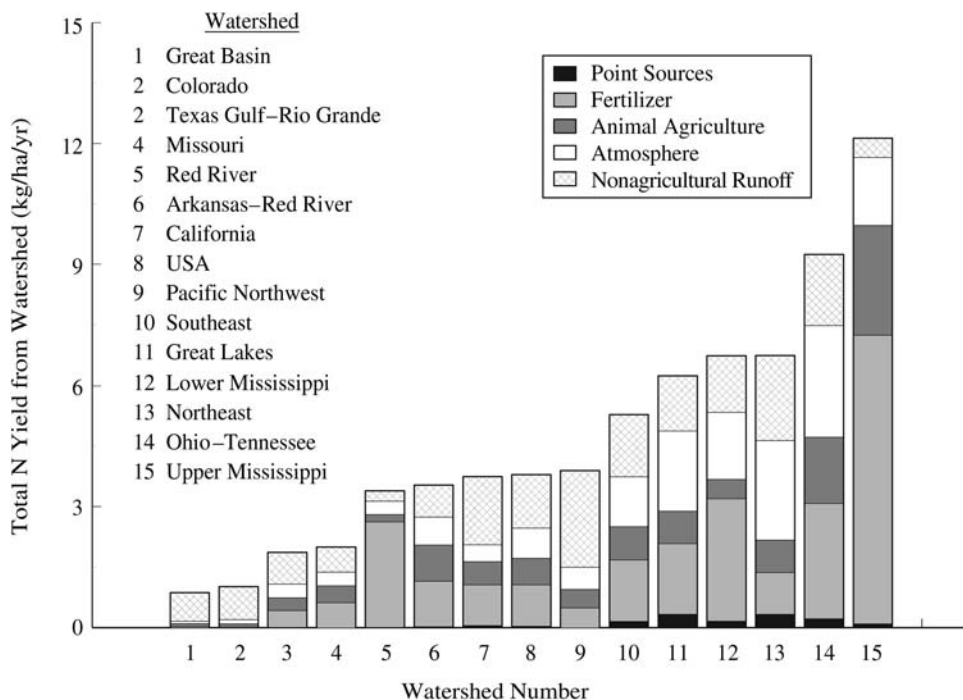


Figure 5.5 Estimated point- and nonpoint-source contributions to annual total N yield from major U.S. watersheds. Total yield is defined as the amount of N (kg N/ha/year) exported from the watersheds in stream flow. (From Sauer, T. J. et al., in R. F. Follett and J. L. Hatfield, Eds., *Nitrogen in the Environment: Sources, Problems, and Management*, Elsevier Science, Amsterdam, 2001. With permission.)

of Mexico. The hypoxic zone in the northern Gulf of Mexico is one of the largest in the world (~20,000 km² of near-bottom waters) and is of the same magnitude as similar areas in the Baltic Sea and Black Sea (Rabalais et al., 2001). Hypoxic waters are characterized by reduced abundance and diversity in biota, direct mortality to fish communities, altered migration patterns, and a decline in habitat quality. Many factors have contributed to the formation of the hypoxic zone in the Gulf of Mexico, including increased riverine discharge of N from agricultural cropland. For example, mean riverine NO₃⁻ concentrations in the Mississippi River basin ranged from 0.14 to 2.9 mg NO₃⁻/N/L at the turn of the 20th century to 0.65 to 6.7 NO₃⁻/N/L in the late 1980s (Goolsby et al., 2001). Stream flow volumes in the MARB have also increased, particularly since the 1950s, likely due to increases in agricultural drainage systems (e.g., tile lines) and more impervious surfaces due to urbanization within the MARB. The combination of higher NO₃⁻ concentrations and greater stream flow has enhanced N discharge from the MARB to the Gulf of Mexico. Reversing the decline in water quality in this important water body first requires an understanding of the geographic origin of the N within this basin. This allows for prioritization of efforts to reduce nonpoint N pollution. Recent models of N discharge from the 42 interior basins of the MARB show marked differences among basins (Figure 5.6a). This study also found that most riverine N was in the NO₃⁻ form (61%), followed by organic N (37%), and NH₄-N (2%). It was estimated that NO₃⁻ flux to the Gulf from the MARB has tripled in the last 30 years, with most of the increase occurring between 1970 and 1983. Agricultural basins dominated by row crop agriculture and high fertilizer and manure N use are the main sources of terrestrial N to the Gulf of Mexico, with some yielding 1500 to 3100 kg N/m²/year (Figure 5.6a). Studies such as these clearly show the need to understand soil N cycling and to develop environmentally efficient agricultural management practices for soil, fertilizer, and organic by-product N use.

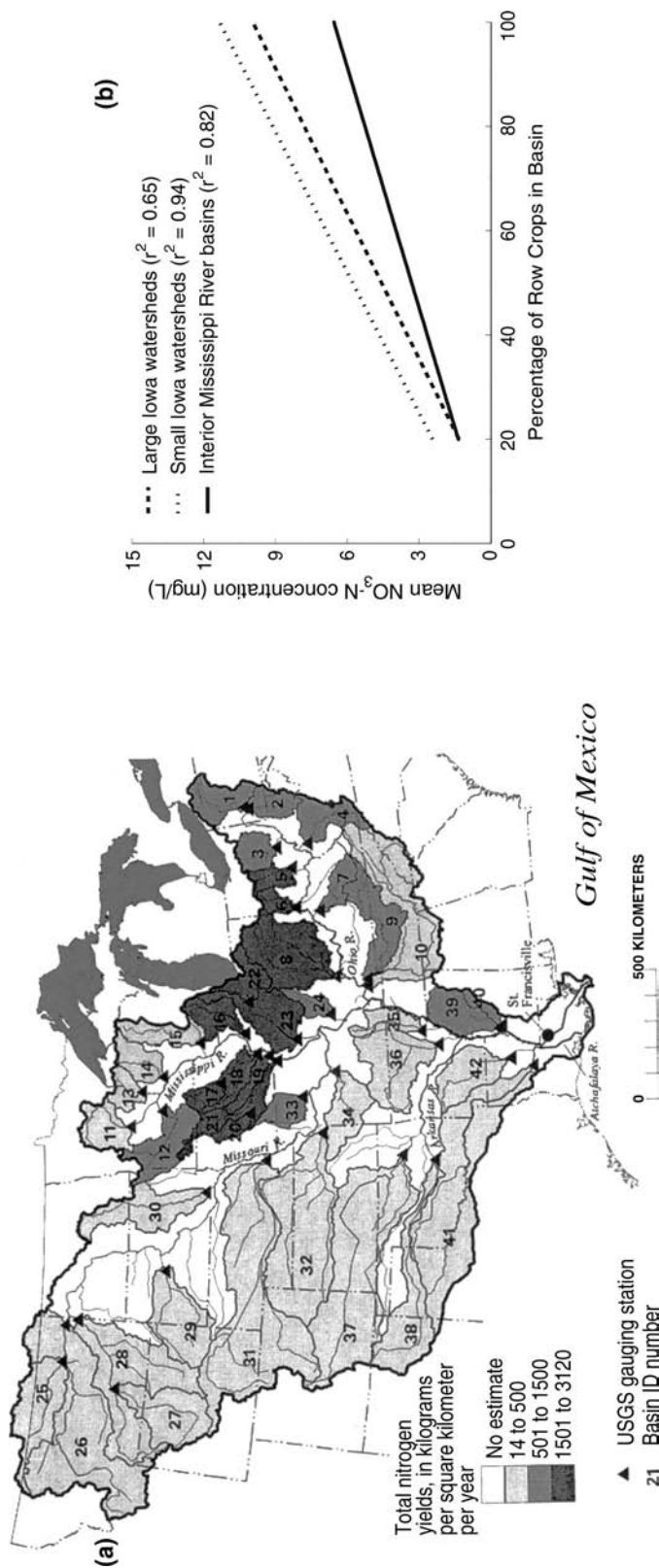


Figure 5.6 (a) Annual total N yields (kg N/km²/year) from 42 sub-basins in the MARB in the United States (From Goolsby, D. A. et al., *J. Environ. Qual.*, 30, 329–336, 2001. With permission.) (b) Relationship between NO₃-N concentrations in streams and the percentage of row crop land in interior Mississippi basins and in small or large watersheds in Iowa. (From Schilling, K. E. and R. D. Libra, *J. Environ. Qual.*, 29, 1846–1851, 2000. With permission.)

5.1.4 Atmospheric Effects of Nitrogen

Nitrogen has been shown to have serious deleterious effects on the Earth's atmosphere and, because of these atmospheric changes, on the quality of terrestrial and aquatic environments. The ultimate cause of the atmospheric problems, and subsequent terrestrial impacts, is the release of *reactive N* (N_r) from the surface of the Earth into the atmosphere. *Reactive N* is defined as "all biologically active, photochemically active, and radiatively active N compounds in the atmosphere and biosphere of the earth." Thus, N_r includes inorganic reduced forms of N (e.g., NH_3 , NH_4^+), inorganic oxidized forms of N (e.g., NO_x , HNO_3 , N_2O , NO_3^-), and organic compounds (e.g., urea, amines, and proteins) (Galloway and Cowling, 2002). Note that, as discussed above, N_r may also be directly released into the lithosphere and hydrosphere without entering the atmosphere, such as by fertilization and manuring of crops, leaching to groundwaters, and stream or point-source discharge to surface waters. It has been estimated that 165 Tg N_r (Tg = terragram = 10^{12} g) are created each year on the Earth: 20 Tg N_r /year are ingested by humans as food, 100 Tg N_r /year are used in agriculture, 25 Tg N_r /year are created by combustion of fossil fuels, and 20 Tg N_r /year are generated by other industries.

Once N_r enters the atmosphere, it can create a series of environmental and ecological problems. Nitrous oxide (N_2O) is a greenhouse gas, and thus increased emissions contribute to global warming (see Chapter 11). Other impacts of N_r are associated with the terrestrial and aquatic deposition of N_r , now a global phenomenon, as shown in Figure 5.7. Nitric acid (HNO_3), primarily caused by the release of nitrous oxides (N_2O , NO) to the atmosphere during burning of fossil fuels, is a major component of *acid deposition*. Studies have shown that acid rain ($\text{pH} < 5.6$), acid mist, or dry deposition of acidic particulates can negatively affect forest ecosystems and surface waters, but the impact on agricultural soils and crops to date has been minimal. Deposition of N_r to soils in natural ecosystems can also cause them to become saturated with N, resulting in losses of biodiversity and the export of N_r to downstream aquatic ecosystems. For example, it has been estimated that up to 35% of Dutch heathlands are becoming dominated by grasses, which are more effective competitors for ecological niches when supplied with additional N via atmospheric deposition. Water quality problems can also occur if N_r is deposited in highly developed areas with large amounts of impervious surface. Many of these trends are illustrated in Figure 5.8 for the Chesapeake Bay watershed in the United States. Deposition of N_r is greatest in the most urbanized regions where fossil fuels are burned by automobiles, to heat homes, and for energy use by industries (the light shaded area in Figure 5.8 near several large U.S. cities, including Washington, D.C., Baltimore, Philadelphia, and New York). Exports of deposited N_r to surface waters are greater from developed and cultivated areas than from forests, and N_r exports are affected by season, being greatest in the spring when stream discharge is at its highest.

Soils can also be negatively impacted by the re-deposition of NH_3 that volatilized from soils or, more significantly, from areas of highly concentrated animal feeding operations (CAFOs). When re-deposited to soils, NH_3 is rapidly converted to $\text{NO}_3\text{-N}$, a process that results in soil acidification (see Section 5.2.1). Acidification of forest soils in Germany by NH_3 originating from the highly concentrated swine, dairy, and poultry operations in the Netherlands has negatively affected some forest ecosystems, causing regional tensions and increased efforts to reduce NH_3 losses from barns, feedlots, and lagoons. Similar trends have been seen in the United States, as shown in Figure 5.9 for coastal North Carolina, where rapid intensification of the swine industry in the 1990s has created a number of environmental problems including concerns about the fate of NH_3 emitted from the thousands of swine operations in this region. Additional information related to acidic deposition can also be found in Chapter 11. As with NO_x , re-deposition of NH_3 can decrease biodiversity and increase N losses to groundwaters and surface waters.

Nitrous oxides have also been shown to increase ozone (O_3) concentrations in the troposphere by reactions with volatile organic compounds (VOCs) and to cause photo-oxidation of O_3 in the stratosphere. Higher O_3 in the troposphere can cause health-related problems in humans (e.g., respiratory

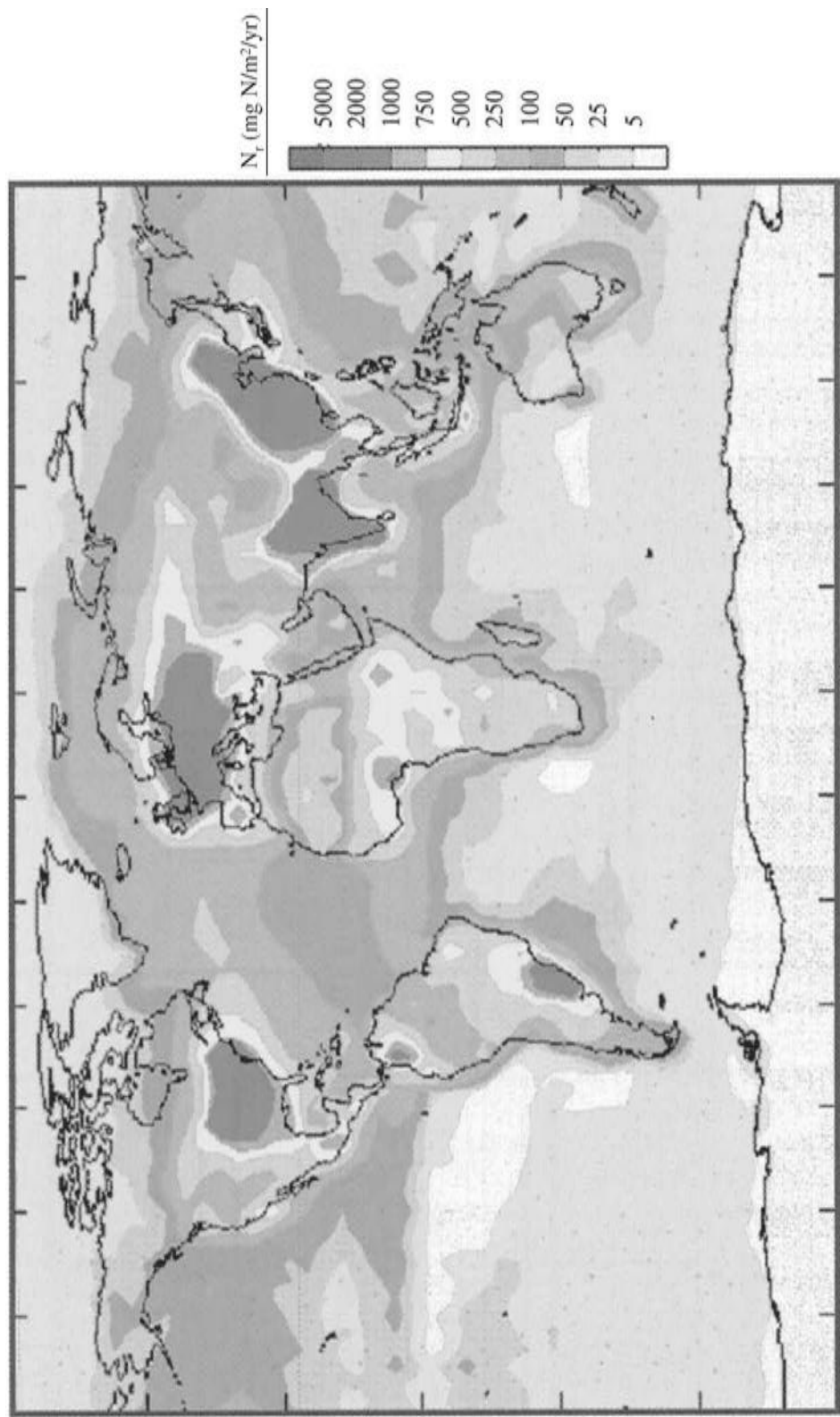


Figure 5.7 (Color figure follows p. 242.) Global deposition of reactive nitrogen (N_r) on the Earth's continents and oceans in 1993. (From Galloway, J. N. and E. B. Cowling, *Ambio*, 31, 64–71, 2002. With permission.)

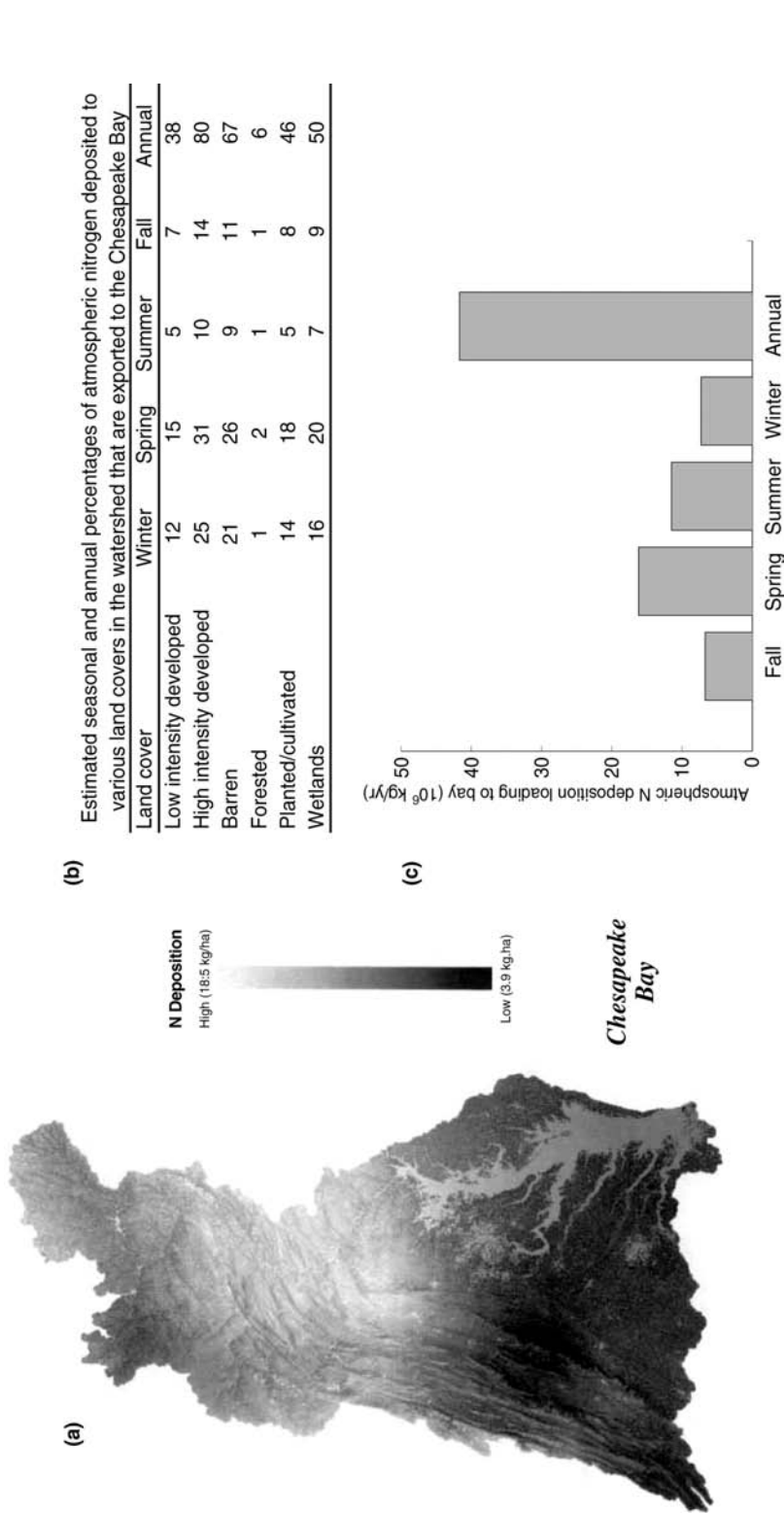


Figure 5.8 (a) Model-generated estimate of atmospheric $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ wet deposition to the Chesapeake Bay watershed; (b) terrestrial land surface export coefficients used to model transport of N from atmospheric deposition to surface water, for various land covers; (c) 12-year average of model-generated seasonal trends in the amount of atmospheric N deposition transported to the Chesapeake Bay from land in the watershed. (From Sheeder, S. A. et al., *J. Environ. Qual.*, 31, 1194–1206, 2002. With permission.)

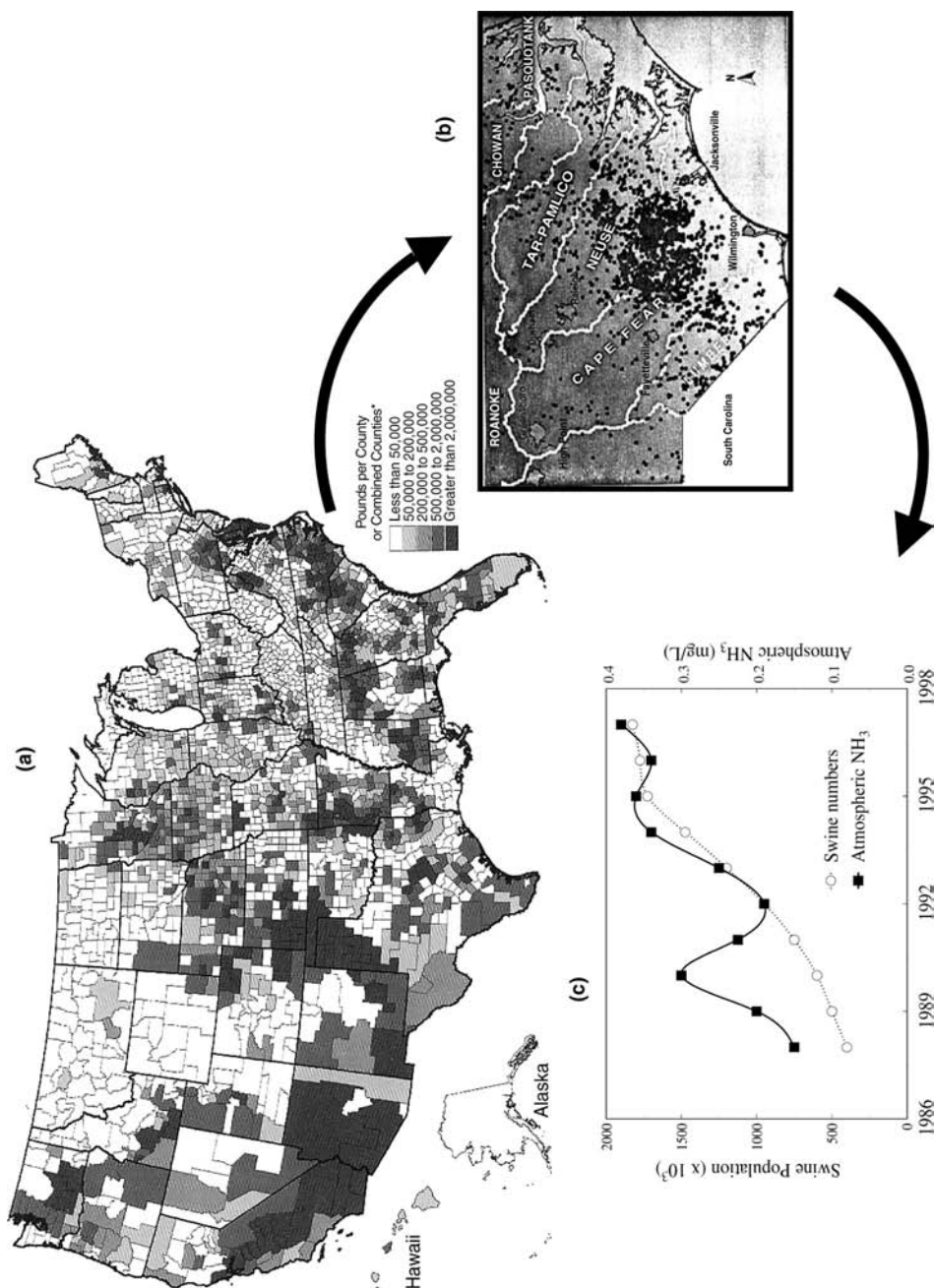
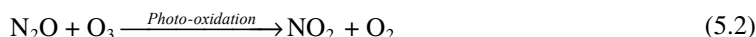


Figure 5.9

(a) Excess manure N in each county of the United States, assuming no export of manure from farms. (From Kellogg et al., 2000.) (b) Geographic concentration of the swine industry in coastal North Carolina (each filled circle is a swine farm.) (From Mallin, M. A., *Am. Sci.*, 88, 26–37, 2000. With permission.) (c) Illustration of the relationship between intensification of swine production in Sampson County, North Carolina from 1986 to 1997 and the increase in atmospheric NH_3 during this time period. (From Mallin, M. A., *Am. Sci.*, 88, 26–37, 2000. With permission.)

illnesses), injure crops, damage buildings and historical monuments, and cause smog to form. Lower O_3 in the stratosphere reduces the capacity of the ozone layer to protect the Earth from the intense ultraviolet radiation emitted by the sun and leads to greater incidences of sunburn, skin cancer, and cataracts.

A simplified version of the reactions of N oxides with ozone is shown below:



In addition to the burning of coal, oil, and gasoline, a major nonpoint source of N_2O and NO is the process of biological *denitrification*, in which soil microorganisms reduce NO_3^- to N_2O under oxygen-limited conditions. *Chemodenitrification* can also occur in soils, resulting in the evolution of NO_x under well-aerated conditions. These processes are discussed in detail in Section 5.2.2.

5.1.5 Risk Assessment for Nitrogen Pollution

It is now widely accepted that N_r generated by anthropogenic activities is a global environmental problem that creates clear risks to humans, animals, and ecosystems. The nature of this risk has been conceptually summarized as the *Nitrogen Cascade* (Figure 5.10). In this approach, two main anthropogenic sources of N_r exist: that generated by food production ($NH_x = NH_3$ and NH_4) and that originating from energy production (fossil fuels). The N_r coming from these two

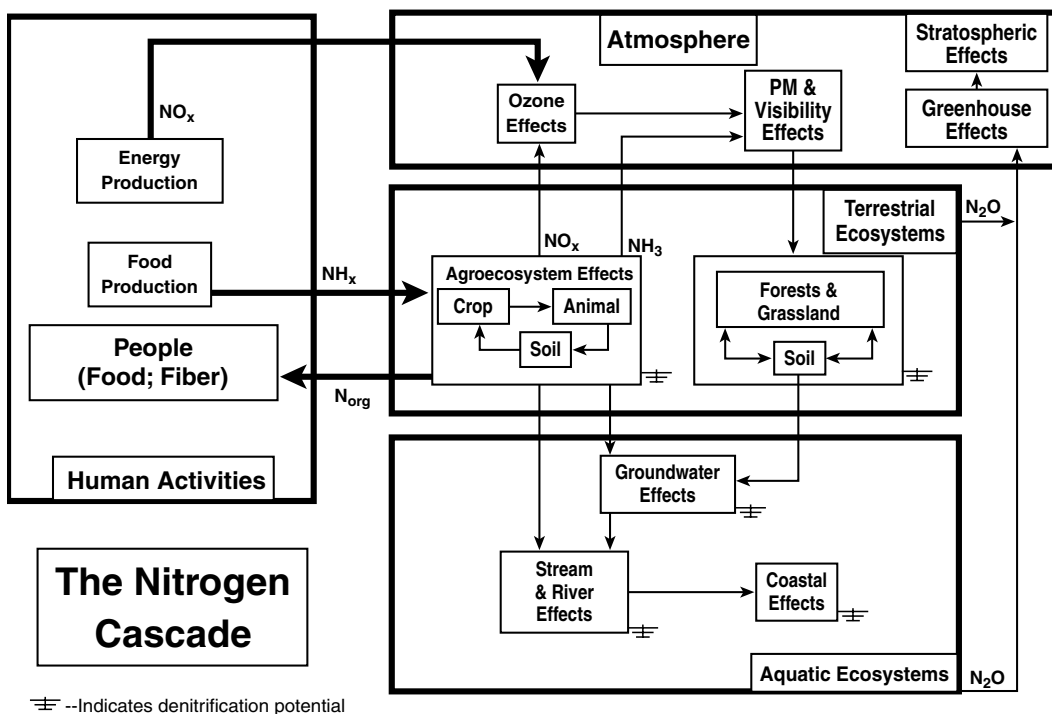


Figure 5.10 The nitrogen cascade, an illustration of the movement of reactive nitrogen (N_r) through the Earth's atmosphere, terrestrial and aquatic environments. (From Galloway, J. N. and E. B. Cowling, *Ambio*, 31, 64–71, 2002. With permission.)

sources “cascades” through the global environment entering atmospheric, terrestrial, and aquatic ecosystems, undergoing transformations in speciation and transfers between ecosystems, with many impacts upon humanity. Some are beneficial, such as the production of food and other useful plants, while others, as described above, are detrimental. Despite decades of research, great uncertainty still exists about the ultimate fate of N_r as it cascades through our environment. We do know that the environmental effects can be quantified on local, regional, and global scales, as illustrated in Figure 5.11, which provides an N budget for Europe. Studying this budget shows that the inputs of N_r from fertilizer production, combustion and industry, and atmospheric deposition (total of 24.6 million Mt/year) far exceeds the capacity of terrestrial and aquatic ecosystems to convert it back to unreactive atmospheric N_2 via denitrification (13.8 million Mt/year). Consequently, N_r cascades into our soils, waters, and back into our atmosphere. Given the limited nature of the resources available to mitigate all forms of pollution and the critical importance of N to food production, proper assessment of the risks associated with N_r is essential to prioritize future efforts to remediate N pollution. The process used for risk assessment is described in Chapter 13, but certain points are apparent at this time with regard to N pollution and soil management.

First, there is a clear public perception that agriculture contributes to N pollution of groundwaters and surface waters by improper fertilization and organic by-product management. While scientific research has substantiated this concern, it has also indicated that groundwater contamination by NO_3^- is often localized in nature and associated with specific regional problems such as well-drained soils, shallow water tables, highly concentrated animal production, intensive irrigation, and by-product or wastewater disposal by municipalities or industry (see Figure 5.4). The combined weight of public perception and scientific documentation assures that the risk of water pollution by N will be addressed by scientific, advisory, and regulatory agencies. In essence, there is sufficient agreement among all parties that risk exists and that a significant commitment of resources to reduce its impacts is needed. A similar consensus is growing that the loss of N_r (e.g., NH_3 and NO_x) from soils and agricultural operations, such as feedlots, to the atmosphere now creates a risk that must be managed.

Second, we must acknowledge that there are significant obstacles to reducing N pollution originating from both agricultural and nonagricultural soils. The pressures to produce increasing

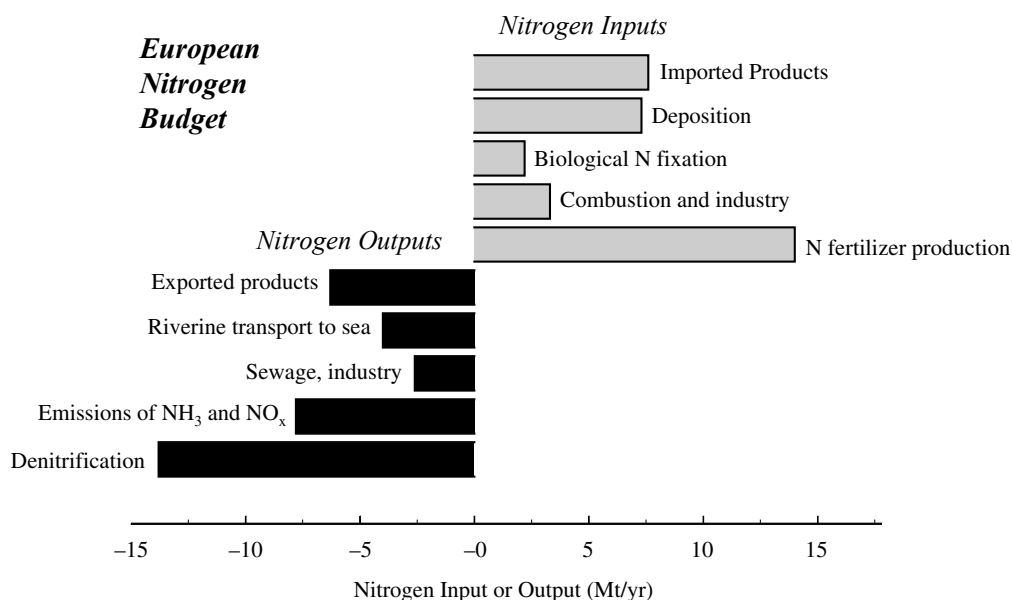


Figure 5.11 An estimated nitrogen budget for Europe (excluding areas belonging to the former Soviet Union). Total N inputs = Total N outputs = 34 Mt N/yr. (From van Egmond, K. et al., *Ambio*, 31, 72–78, 2002. With permission.)

amounts of food with fixed amounts of arable land often result in the use of higher and often less efficient N rates as we substitute fertilizer N for soil N. The need to maintain farm profitability and the low costs of fertilizer N favor the use of insurance fertilization to overcome unexpected N losses that may be caused by uncontrollable climatic events. The nature of modern animal-based agriculture concentrates nutrients derived from soils, fertilizers, and organic N in other regions into areas without an adequate land base for proper N use. A similar scenario exists for organic by-products produced in cities (e.g., biosolids). Conversion of grasslands and forests to agricultural land for the production of annual crops can release organic N stored for centuries over a relatively short period of time, enhancing the potential for enrichment of groundwaters and surface waters with NO_3^- . Recreational developments near sensitive water bodies can discharge N from septic systems into groundwaters; overfertilization of turf in urban areas can produce runoff high in NO_3^- . It is apparent that the technology, education, effort, and cost required to design and implement improvements in N management for each of these scenarios are formidable. Prioritization of risk thus becomes critically important to the allocation of resources.

Finally, it is also important to acknowledge the time required to correct the problem. Groundwaters that have been contaminated with NO_3^- by land use practices over a 30-year period are likely to require several decades to “dilute” to acceptable concentrations with the low NO_3^- leachate coming from soils receiving improved management practices. This means that the cost of reducing N pollution of our natural waters must be borne by society for many years, and that a long-term, integrated effort between all responsible parties will be needed.

5.2 THE SOIL NITROGEN CYCLE

The soil nitrogen cycle (Figure 5.2) is a subset of the global N cycle (Figure 5.1) and can be viewed as a conceptual summary of the interactions among the chemical, physical, and biological transformations of N in soils. This chapter focuses on environmental concerns related to soil N; hence the interactions of the soil N cycle with the segments of the environment most sensitive to pollution by N (groundwaters, surface waters, the atmosphere) are emphasized. From this perspective, the key N transformations are the cycling of N between organic and inorganic forms (*mineralization and immobilization*), gaseous losses of N to the atmosphere (*ammonia volatilization and denitrification*), losses associated with water movement (*leaching and erosion*), and *biological N fixation*. Many of these reactions are controlled by soil microorganisms that alter the form and oxidation states and, thus, the fate of N between N_2 , N_2O (nitrous oxide), $\text{NH}_3/\text{NH}_4^+$ (ammonia/ammonium), NO_2^- (nitrite), and NO_3^- (nitrate). It is critical to recognize, from a management standpoint, how the relative importance of each reaction varies with soil and environmental conditions and when it is possible to exert a significant degree of control over a given reaction. Our ability to control an N transformation, however, will depend not only on the biology, chemistry, or physics of the process, but also on the intensity and economics of management. Farmers using irrigation, for example, have more control over the timing of N delivery to crops than those in dryland agriculture because of their ability to inject soluble N fertilizers into irrigation waters. This can improve the crop N use efficiency, reducing NO_3^- leaching. Industries involved in land reclamation or municipalities charged with biosolids disposal may increase the extent of by-product processing (e.g., composting or lime stabilization) due to greater regulation on organic by-product use related to pathogens, metals, or organic pollutants. These changes in by-product properties may then affect the N transformations likely to occur upon land application of the by-product material.

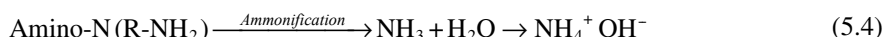
Sound environmental management of N begins with an understanding of the major components of the soil N cycle. Enormous scientific effort has been expended to study N transformations in

soils. The challenge now is to translate this knowledge into practical management programs that achieve both production and environmental goals. In the following sections the basic principles underlying each of the key N transformations are described, and in later sections of this chapter techniques that can be used to manage these N transformations will be related to agricultural, urban, and land reclamation issues.

5.2.1 Mineralization, Nitrification, and Immobilization of Nitrogen

Mineralization refers to the microbial conversion of organic forms of N (e.g., proteins, chitins, amino sugars from microbial cells, and nucleic acids) to inorganic N, as ammonium-N (NH_4^+). The organic N may be indigenous to the soil or freshly added as crop residues, animal manures, or municipal by-products. Most (>95%) of the N in soils is organic in nature; hence microbial conversion of organic N to plant-available forms (NH_4^+ , NO_3^-) is important for the growth of all plants, especially those in native ecosystems where anthropogenic sources of N are normally not added to soils. Soils also contain soluble forms of organic N that are available for plant uptake. Although the exact chemical composition of soluble organic N is not clear, it can be found in soils at concentrations similar to or even greater, in the case of manured or grassland soils, than inorganic N (~0.3 to 1.5% of total organic N).

The soil N mineralization process is mediated by a diverse population of heterotrophic soil microorganisms (i.e., bacteria, fungi, actinomycetes) that produce a wide variety of extracellular enzymes capable of converting proteins (proteinases, peptidases) and nonproteins (chitanases, kinases) into NH_4^+ . These microbes use the energy derived from the oxidation of soil organic matter for metabolic activities and the N released during decomposition to produce the amino acids and proteins essential for population growth. The reactions involved in mineralization of organic N to inorganic NH_4^+ can be summarized as follows:



Once mineralized, NH_4^+ can be taken up by plants, nitrified, immobilized by soil microorganisms, lost as a gas by ammonia volatilization, held as an exchangeable ion by clays or other soil colloids, or fixed in the interlayers of certain clay minerals. Each of these potential fates of NH_4^+ is described later in this chapter.

Mineralization of N from soil organic matter can provide a significant portion of the N requirement of some plants, but will be far from adequate to achieve economically optimum yields with many agricultural crops. Plants can absorb NH_4^+ directly from the soil solution and, in fact, studies have shown that NH_4^+ is taken up preferentially by some plants over other sources of N (e.g., NO_3^-). In general, however, NO_3^- uptake by plants is greater than NH_4^+ because NO_3^- is usually present at higher concentrations in the soil solution and moves more freely to plant roots by mass flow and diffusion than NH_4^+ . Total N values for topsoil horizons of most mineral soils range from 0.05 to 0.15%. Under well-aerated conditions about 1 to 3% of the organic N component of soil total N will mineralize annually, producing ~15 to 70 kg N/ha per year. In comparison, fertilizer N recommendations for many annual, nonleguminous crops range from ~50 to 200 kg N/ha. Long-term use of animal manures or leguminous rotational crops such as alfalfa can greatly increase the amount of potentially mineralizable organic N in soils. As discussed in more detail in Chapter 8, this can result in marked reductions in fertilizer N requirements, an important consideration from economic and environmental perspectives.

Example Problem 5.2

The A horizon of a soil (0 to 15 cm) has a total N concentration of 0.100 and 95% of the total N is organic N. How much N, in kg/ha, will be mineralized from soil organic N during the growing season of an annual row crop such as corn (~120 days)? Assume that there are 2.24×10^6 kg soil in a hectare to a depth of 15 cm and that there is a constant annual organic N mineralization rate of 2%.

$$\text{Total N in soil} = 0.100\%$$

$$\text{Total N in soil (kg/ha)} = (0.001) \times (2.24 \times 10^6 \text{ kg soil/ha}) = 2240 \text{ kg } N_t/\text{ha}$$

$$\text{Organic N in soil} = (0.95) \times 2240 \text{ kg N/ha} = 2128 \text{ kg } N_o$$

$$\text{Mineralized N (kg/ha)} = (2128 \text{ kg } N_o/\text{ha}) \times (0.02) \times (120/365)$$

$$\text{Mineralized N (kg/ha)} = 14 \text{ kg N/ha}$$

The timing of N mineralization, relative to the timing of crop N uptake, can be as important a consideration as the amount of N mineralized. Most studies have shown that under optimum conditions N mineralization follows a curvilinear pattern, as illustrated in Figure 5.12a. The amount of *potentially mineralizable organic N* in soils (N_o) and the rate of N mineralization (k) have been successfully described by relatively simple first-order kinetic models that relate the change in mineralized N (N_m) in soils with time (dN_m/dt) to the amount of mineralizable substrate (N_o) as follows:

$$dN_m/dt = k(N_o) \quad (5.5)$$

Data from laboratory studies measuring the amount of NH_4^+ and NO_3^- leached or extracted from soils at differing time intervals (N_m , t) can be used with the integrated form of this equation to estimate N_o and k for different soils, as a function of soil horizon, changing soil chemical and environmental conditions (e.g., pH, temperature, moisture), or as affected by long-term changes in soil N due to tillage practices, fertilizer applications, or applications of organic by-products. Ideally, if N_o and k are known, the amount of mineral N in the soil after a specified time interval could be predicted as

$$N_m = N_o (1 - e^{-kt}) \quad (5.6)$$

Some research has shown that a model based on two pools of N_o (N_f = “fast” mineralization of readily decomposable organic N and N_s = slow mineralization of recalcitrant organic N) with separate rate constants for mineralization of each pool (k_f for N_f , k_s for N_s) better describes the results of N mineralization studies, particularly for soils amended with organic N sources (Figure 5.12b):

$$N_m = N_f (1 - e^{-k_f t}) + N_s (1 - e^{-k_s t}) \quad (5.7)$$

Nitrification is the conversion of NH_4^+ into nitrite (NO_2^-) and then NO_3^- by the actions of obligately aerobic, chemoautotrophic bacteria (i.e., obtain carbon from CO_2 or carbonates and energy from the oxidation of NH_4^+ or NO_2^-). Initially, bacteria of the genus *Nitrosomonas*, *Nitrospira*, or *Nitrococcus* oxidize NH_4^+ to hydroxylamine (NH_2OH) and then, through several

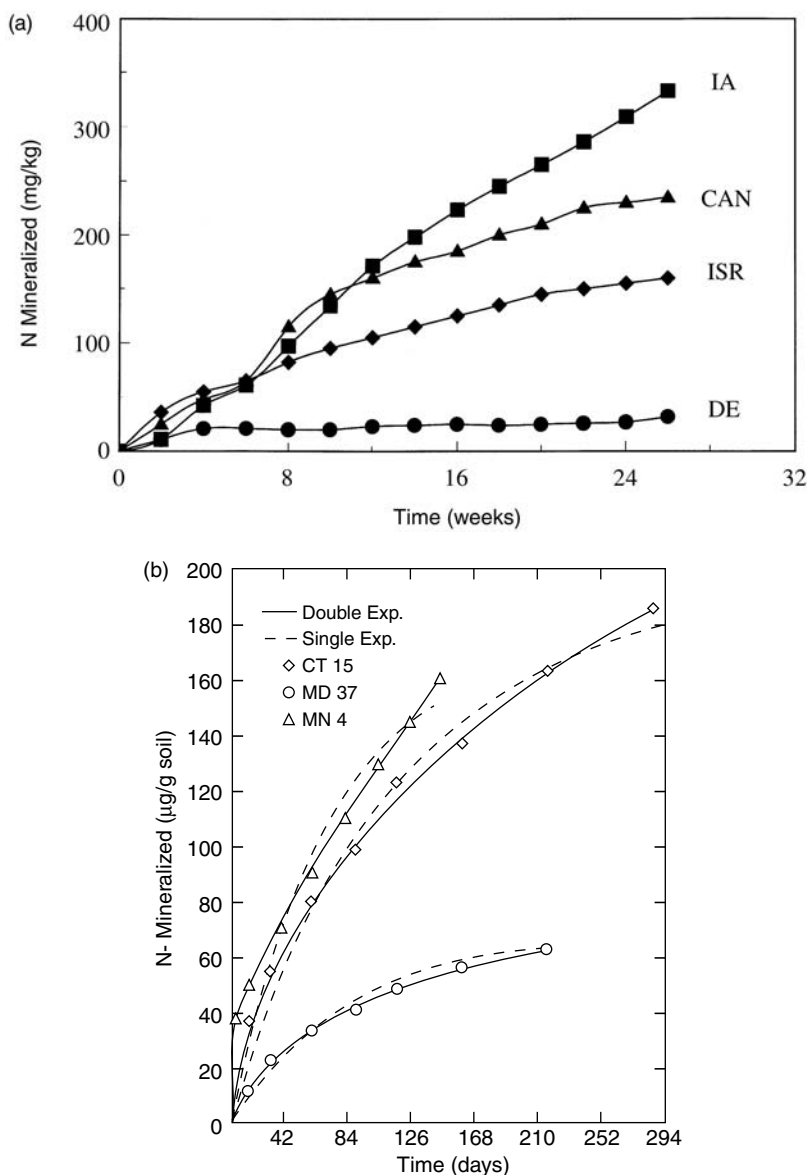


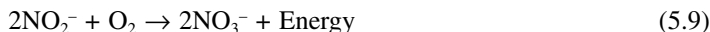
Figure 5.12 (a) Nitrogen mineralization patterns for different soils. [Adapted from laboratory studies conducted by Chae and Tabatabai, 1986 (Iowa, IA); Ellert and Bettany, 1988 (Canada, CAN); Hadas et al., 1983 (Israel, ISR); and Sallade and Sims, 1992 (Delaware, DE).] (b) Comparison of single and multiple substrate models simulate N mineralization in a sludge-amended soil. (From Deans, J. R. et al., *Soil Sci. Soc. Am. J.*, 50, 323–326, 1986. With permission.)

intermediate compounds that are not as well known, to NO_2^- . Key features of this step are the change in oxidation state of N from -3 to $+3$, and soil acidification by hydrogen ions (H^+) produced when NH_4^+ is oxidized:



In the next reaction, bacteria of the genus *Nitrobacter*, *Nitrospira*, or *Nitrococcus* continue the oxidative process, convert NO_2^- to NO_3^- , and change the oxidation state of N from $+3$ to $+5$. Rapid

conversion of NO_2^- to NO_3^- is important because of the toxicity of NO_2^- to plants and animals, even at very low concentrations in soils.



Nitrate can then be used directly by plants or soil microorganisms or lost from the crop rooting zone by *denitrification*, *leaching*, or *erosion/runoff* (Sections 5.2.2 and 5.2.3). In most soils, nitrification is a rapid process, which is somewhat unfortunate given the much greater mobility in soils of NO_3^- than NH_4^+ . Chemical inhibitors of nitrification can delay this conversion process and have been shown in laboratory studies to be quite effective (see Figure 8.12). To date, however, field research on the effectiveness and economic value of nitrification inhibitors for fertilizers and organic by-products has been inconclusive.

Immobilization is essentially the reverse of mineralization, and involves the assimilation of inorganic N (NH_3 , NH_4^+ , NO_2^- , NO_3^-) by soil microorganisms and the transformation of these mineral forms of N into organic compounds during microbial metabolism and growth. Plant uptake can also be viewed as a form of immobilization, and understanding or controlling the competition between plants and soil microorganisms for inorganic soil N is an important aspect of soil N management. As immobilization represents the formation of organic nitrogenous compounds, it will be controlled to a large extent by the availability of the carbon (C) needed to produce amino acids and proteins. If a large supply of available C is present in the soil, relative to inorganic N, microbial growth and consumption of soluble N will be stimulated, thus enhancing the conversion of soluble N into biomass N. Lower ratios of available C to N will result in an excess of NH_4^+ or NO_3^- in the soil, relative to microbial requirements. The carbon:nitrogen ratio (C:N) of native or added organic matter, along with environmental conditions that regulate microbial population growth, will thus control the amount of inorganic N available for plant uptake or other less desirable fates (leaching, denitrification). Stable soil organic matter has C:N ratios from 10:1 to 12:1, while soil organisms have C:N ratios of from 5:1 to 8:1. Mineralization of soil organic matter provides adequate C and N for soil microorganisms and, as mentioned above, a small to moderate quantity of available N for plant uptake. Adding organic amendments with differing C:N ratios to soils, however, can cause significant but reasonably predictable changes in the amount of plant-available inorganic soil N, as illustrated by eight studies on N mineralization from crop residues with C:N ratios ranging from 8:1 to 80:1 (Figure 5.13a). A C:N ratio of ~25:1 (organic matter that is 40% C and 1.6% N) is commonly used as the ratio where mineralization and immobilization are in balance. Adding materials with wide (>30:1) C:N ratios (straw, sawdust, papermill sludges) can cause a rapid increase in microbial biomass and a depletion of available soil N to the point where N deficiency can occur in many plants. Conversely, some organic amendments (e.g., biosolids, poultry manure) with very low C:N ratios can produce large excesses of soluble N and must be managed carefully to avoid N losses to sensitive parts of the environment. Composting is an effective way of stabilizing N in rapidly mineralizable organic by-products, as shown in Figure 5.13b. Careful attention to plant N nutrition is required when composts are used; however, as soils amended with composts often exhibit an initial period of N immobilization and then release N more slowly than the rate required by plants. The C:N ratio of added organic matter does not remain constant during the decomposition process as C from microbial respiration is evolved from the soil as CO_2 . With time, the C:N ratio will decrease into the range where mineralization, not immobilization, predominates and the soil once again provides some available inorganic N for plant uptake.

Given the importance of soil microorganisms in mineralization, nitrification, and immobilization reactions, it is apparent that proper management of soil N, particularly from organic sources (crop residues, manures, biosolids), requires an understanding of the soil and environmental factors that can affect the activity of microorganisms controlling these reactions. All parameters that affect biological activity (i.e., temperature, moisture, aeration, and soil pH) have been shown to influence the rate and extent of these three N transformations. "Optimum" conditions for each transformation

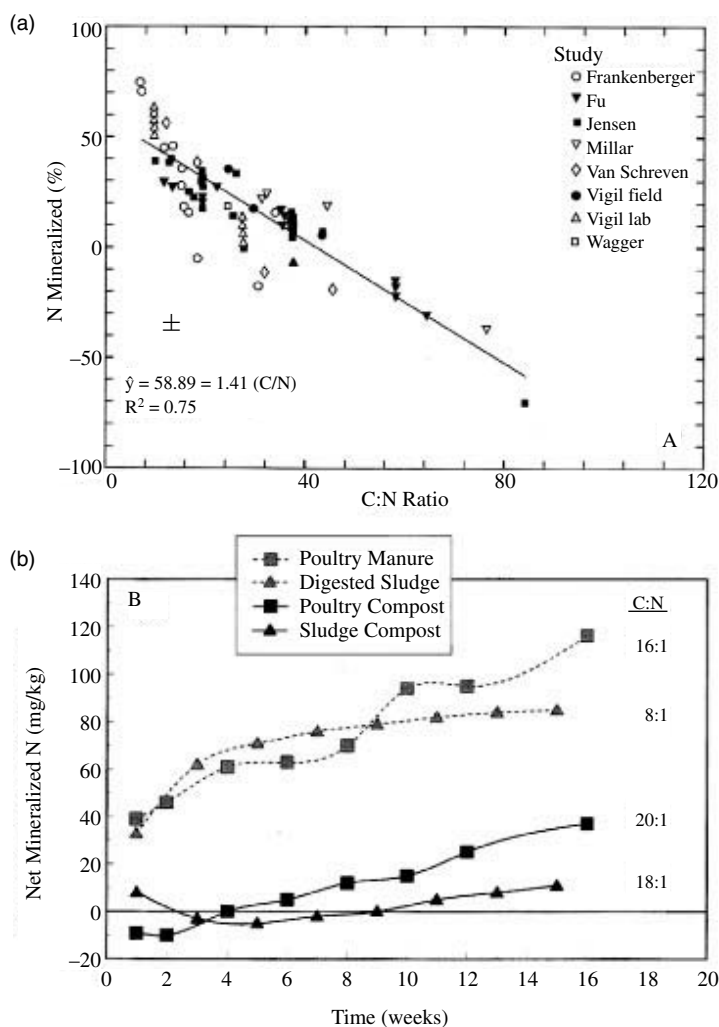


Figure 5.13 (a) Effect of C:N ratio of crop residues on N mineralization. (From Vigil, M. F. and D. E. Kissel, *Soil Sci. Soc. Am. J.*, 55, 757–761, 1991. With permission.) (b) Effect of composting digested sewage sludge (biosolids) or poultry by-products on N mineralization. (Adapted from Epstein et al., 1978; Sims et al., 1992.)

have been broadly defined and vary slightly between mineralization–immobilization reactions and nitrification. Because a much wider variety of organisms participate in mineralization and immobilization, these processes are somewhat less sensitive to changing environmental conditions than nitrification. As an example, unlike nitrification, mineralization can proceed under anaerobic conditions and at much wider temperature ranges. This can result in an accumulation of NH_4^+ in flooded soils where nitrification is inhibited by a lack of oxygen, or under extreme soil temperature regimes ($<5^\circ\text{C}$ or $>40^\circ\text{C}$). For mineralization and immobilization, the optimum conditions are a temperature range of 30 to 40°C , with a Q_{10} (change in reaction rate when temperature increases 10°C) of about 2.0, and a soil moisture content of 50 to 75% of soil water-holding capacity, although the actual optimum moisture percentage varies with soil texture (Table 5.2). For nitrification, optimum conditions include temperatures of 30 to 35°C , a moisture content of 50 to 67% of soil water-holding capacity, and a pH between 6.6 and 8.0. Nitrifying organisms are more sensitive to excessive soil acidity and their activity decreases markedly when the soil pH is less than 5.0, resulting in the accumulation of NH_4^+ in such soils. Consequently, plants that are well

Table 5.2 Influence of Soil Temperature and Moisture on N Mineralization

Soil Temperature (°C)	Nitrogen Mineralization Rate Constant (k , wk ⁻¹)	
	Range for 11 Soils	Mean
5	0.007–0.015	0.009
15	0.010–0.022	0.014
25	0.019–0.047	0.029
35	0.044–0.071	0.055

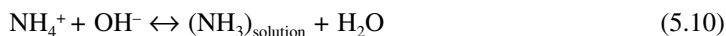
Soil Moisture Tension (MPa)	Total N Mineralized at 35°C (mg/kg)	
	Fine Sandy Loams	Loams to Clay Loams
0.01	39	71
0.03	36	67
0.20	29	50
1.50	26	43
Estimated Optimum Soil Moisture Content (%):	13	28

Sources: Adapted from Stanford et al., 1973 (temperature); Stanford and Epstein, 1974 (moisture).

adapted to acidic soils (e.g., coniferous forests) or flooded soil conditions (e.g., rice) are believed to primarily absorb NH_4^+ from the soil solution.

5.2.2 Gaseous Losses of Nitrogen: Ammonia Volatilization and Denitrification

Ammonia volatilization refers to the loss of NH_3 from the soil as a gas and is normally associated with high free NH_3 concentrations in the soil solution and high soil pH. Surface applications of ammoniacal fertilizers or readily decomposable organic by-products (manures, biosolids) to soils can also result in considerable N loss by NH_3 volatilization, particularly if the soil (or organic by-product) is alkaline in nature. This reaction and the major factors influencing the magnitude and rate ($d[\text{NH}_3]/dt$) of N loss by volatilization can be summarized as follows:



and

$$\frac{d[\text{NH}_3]}{dt} = [A] \times [K] \times [P_l - P_g] \quad (5.12)$$

where

$$\frac{d[\text{NH}_3]}{dt} = \text{NH}_3 \text{ loss in time (t)}$$

- A = area of soil–solution interface
- K = mass transfer coefficient, a function of air velocity above the soil and the air and soil temperatures
- P_l = partial pressure of NH_3 in soil solution
- P_g = partial pressure of NH_3 in air above soil solution

Volatilization represents both the loss of a plant nutrient and a potential environmental impact as surface waters can be enriched by deposited NH_3 that is volatilized from areas where organic by-products are concentrated (e.g., feedlots, lagoons); soils can also be acidified when the NH_3 deposited is nitrified. For example, a study in England (Pitcairn et al., 1998) found that NH_3 emissions from livestock operations adversely affected flora in nearby woodlands (<300 m from NH_3 source). The number of natural species in the woodland decreased and “weedy” species increased. A “critical depositional load” of >20 kg N/ha was identified, above which undesirable changes in species diversity occurred. Similar changes in biodiversity were reported for Dutch forests and heathlands located on sandy, low-organic-matter, nutrient-deficient soils. Native vegetation in these natural ecosystems was adapted to low soil fertility conditions, but in the mid-1980s changes in species diversity began to be observed. At the same time, N deposition increased to as much as 40 to 80 kg N/ha/year (as NH_3 and NO_x). Plants previously confined to arable land, such as grasses, began to expand because they could survive and outcompete native vegetation once soil N levels increased. Several species of “nitrophilous” (N-loving) lichens that had been rare reappeared in forests. Some researchers estimated N deposition would have to decrease to about 6 kg N/ha/year for “low N” ecosystems to recover (van Breemen and van Dijk, 1988).

Example Problem 5.3

Monitoring stations in a forest near a large animal feedlot found that 30 kg N/ha volatilized as NH_3 from the animal production area was deposited in the forest each year. If it takes 3 kg of agricultural limestone to neutralize the acidity produced by 1 kg of NH_3 , how much lime would be needed, in kg/ha/year, to prevent acidification of forest soils from re-deposited NH_3 ?

$$\text{Total N deposited} = 30 \text{ kg N/ha/year}$$

$$\text{Molecular weight of } \text{NH}_3 = [14 + 3(1)] = 17$$

$$\% \text{N in } \text{NH}_3 = (14/17) = 0.82 \text{ (82\%)}$$

$$\text{kg of } \text{NH}_3 \text{ added} = (30 \text{ kg N/ha/year})/(0.82) = 36.5 \text{ kg } \text{NH}_3/\text{ha/year}$$

$$\text{Limestone needed} = (36.5 \text{ kg } \text{NH}_3/\text{ha/year}) \times (3 \text{ kg lime/kg } \text{NH}_3) = 108 \text{ kg limestone/ha/year}$$

As described above, the key factors in the volatilization of NH_3 from soils are those that affect: (1) soil pH, which controls the concentrations of OH^- ions in solution (as pH increases, higher OH^- concentrations in the soil solution favor conversion of the more stable NH_4^+ cation to the volatile, gaseous form NH_3); (2) the transfer of a gas between the soil solution and the atmosphere (area of solution–atmosphere interface, velocity of air across the soil surface); and (3) the general rate of a chemical reaction (temperature, partial pressure of NH_3 in both phases).

Soil and management factors that control these aspects of NH_3 volatilization include soil temperature, moisture, and texture, nature of N source, and methods of application of fertilizers or organic by-products (e.g., surface broadcast, injected, incorporated). Conditions associated with maximum NH_3 volatilization will include surface applications of fertilizers or manures, high pH or calcareous soils, soils with low cation exchange capacities and therefore little ability to retain the NH_4^+ cation, and a warm, slightly moist environment. Volatilization losses also increase as soils, or surface-applied organic by-products with high NH_3 concentrations, dry out because removal of water from soils favors the conversion of NH_4^+ to NH_3 (see Equation 5.10). Volatilization is a particular problem for pastures, turf, and no-tillage agriculture where surface applications of fertilizers and manures are required.

In general, the most effective method to reduce NH_3 volatilization losses is to incorporate the N source into the soil by tillage, injection, irrigation, or, through timing N source application to coincide with natural rainfall, as shown in Figure 5.14, Figure 5.15, and Table 5.3. As shown

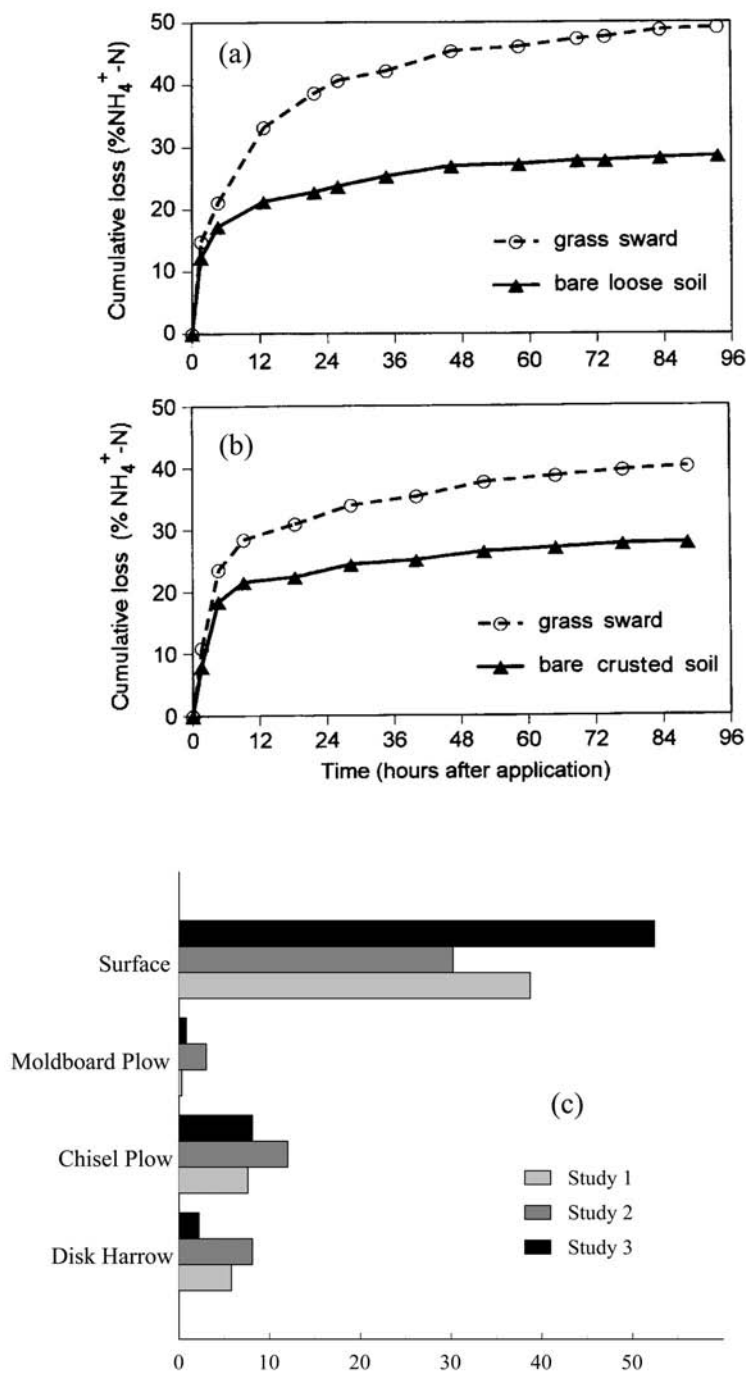


Figure 5.14 Volatilization losses of NH_3 from cattle slurry: (a) applied to a tall fescue grass sward or bare loose soil; (b) applied to a tall fescue grass sward or bare crusted soil; (c) as affected by method of immediate incorporation of the slurry compared to surface application without incorporation. (From Thompson, R. B. and J. J. Meisinger, *J. Environ. Qual.*, 31, 1329–1338, 2002. With permission.)

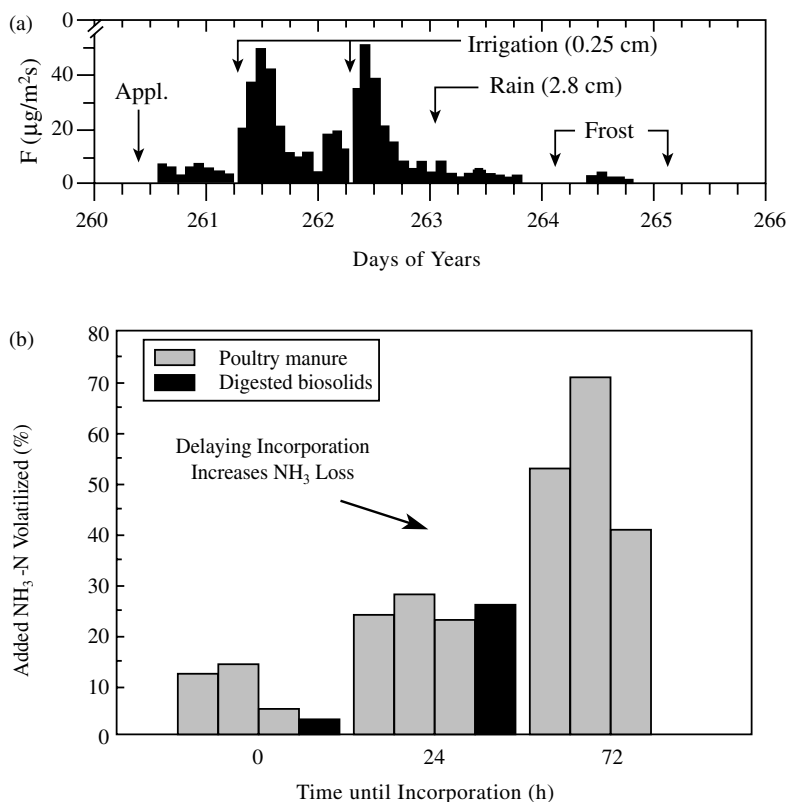


Figure 5.15 (a) Volatilization of NH_3 from urea applied to a moist, bare soil surface. Initial rate of volatilization (F) is slow. Application of low rate of irrigation (0.25 cm) dissolves urea, enhances NH_3 loss until soil surface dries (days 261–262). Second irrigation results in similar pattern of NH_3 loss as soil wets and dries. Rainfall (2.8 cm) on day 263 leaches NH_3 into soil and volatilization rate decreases markedly. (From McInnes, K. J. et al., *Agron. J.*, 78, 192–196, 1986. With permission.) (b) Effect of time between application of poultry manure and digested sewage sludge on NH_3 losses from soils. (Adapted from Donovan and Logan, 1983; Gartley and Sims, 1993.)

in Figure 5.14a and b, about 40 to 50% of $\text{NH}_4^+\text{-N}$ applied in cattle slurry to a tall fescue grass pasture was lost by volatilization within 3 days of application. This was about 1.5 times as much NH_3 loss as occurred when the slurry was applied to a bare soil, probably because some of the liquid slurry could infiltrate into the bare soil. Incorporation of the cattle slurry into the soil, by any tillage method, greatly reduced NH_3 loss (Figure 5.14c). Similar effects of incorporation were seen with poultry manure and biosolids (Figure 5.15). Once incorporated by tillage, or after liquid materials infiltrate into soils or are leached into soils by rainfall, the cationic nature of NH_4^+ results in its electrostatic attraction to cation exchange sites on clays and organic matter, thus reducing NH_3 losses. In soils dominated by 2:1 clay minerals (e.g., vermiculite), NH_4^+ can also be “fixed” in a nonexchangeable, slow-release form, because its size allows it to diffuse into the interlayers of these clays. Fixed NH_4^+ concentrations are usually greater in subsoils, where clay content is higher, and can account for from 20 to 40% of total subsoil N in soils with high amounts of 2:1 clays.

Urea [$\text{CO}(\text{NH}_2)_2$] fertilizers and uric acid found in manures and other organic by-products represent a special case of NH_3 volatilization. When urea is added to a soil it is decomposed in a reaction that is catalyzed by the enzyme urease (urea amidohydrolase), as shown below:

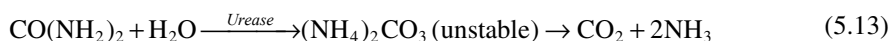


Table 5.3 Effect of Application Method and Rainfall on Corn Yields Where Volatile Ammonia-Based Fertilizers (UAN, Urea) Were Used

Effect of Application Method					
N Source	Application Method	Corn Yield (Mg/ha)			
		N Rate (kg/ha)			
		90	180	270	Mean
UAN	Broadcast spray	5.6	6.8	7.2	6.5
	Surface band	7.4	8.3	8.7	8.1
	Incorporated band	7.9	8.8	8.7	8.5

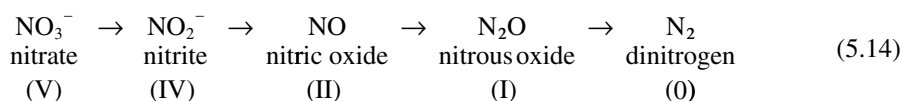
Effect of Rainfall					
N Source	Rainfall	Corn Yield (Mg/ha)			
		N Rate (kg/ha)			
		50	101	202	Mean
NH ₄ NO ₃	25 mm within 36 h of application	10.1	11.3	11.6	11.0
Urea	25 mm within 36 h of application	10.4	11.7	11.2	11.1
NH ₄ NO ₃	None for 3 days then 3 mm	8.8	10.7	11.1	10.2
Urea	None for 3 days then 3 mm	8.5	9.2	10.4	9.4

Note: In rainfall effects study, NH₄NO₃ represents a stable N source with low volatilization potential.

Source: Adapted from Touchton and Hargrove, 1982 (application method); Fox and Hoffman, 1981 (rainfall effects).

Urease is produced by soil microorganisms involved in the decomposition of soil organic matter, in crop residues, and other organic materials. Urease acts by rapidly hydrolyzing the C–NH₂ bonds in the urea molecule. The rapid formation of a highly concentrated solution of NH₄⁺ in the microenvironment surrounding adjacent urea granules increases the pH to about 8.5, greatly enhancing volatilization of NH₃. Chemical inhibitors of the urease enzyme have been developed to reduce the rate of urea hydrolysis and thus the potential for N losses by NH₃ volatilization.

Denitrification is defined as the reduction of NO₃[–] to gaseous forms of N (NO, N₂O, N₂) mainly by heterotrophic (obtain energy and C from oxidation of organic matter) bacteria, such as *Pseudomonas*, *Bacillus*, *Micrococcus*, and *Achromobacter*. Some autotrophic bacteria (obtain energy from oxidation of inorganic elements) are also denitrifiers, such as *Thiobacillus denitrificans*, which obtains the energy needed for denitrification from sulfide oxidation. The main steps in the denitrification process, and oxidation states of the various N species, are as follows:



The bacteria responsible for denitrification are primarily *facultative anaerobes* that normally use O₂ for respiration. However, under anaerobic conditions, they can use NO₃[–] as an alternative acceptor of electrons produced during organic matter decomposition (or sulfide oxidation). During the denitrification process, N is reduced from an oxidation state of +5 in NO₃[–] to 0 in N₂. The O₂ released from NO₃[–] during denitrification normally reacts with C released from organic matter to form CO₂.

The critical factors regulating the rate and duration of denitrification in soils are the availability of NO_3^- (the substrate) and C (source of energy and electrons) and the absence of O_2 . For denitrification to occur, soils must first produce or be amended with NO_3^- and then enter an anaerobic period ($<10\%$ O_2 in soil atmosphere). Conversely, denitrification can be inhibited by any process that restricts NO_3^- production (e.g., slows nitrification), enhances NO_3^- removal (leaching, plant uptake), or promotes aerobic conditions (artificial drainage, plant depletion of soil moisture). Soil temperature and pH can also influence denitrification, which can occur at temperatures between 2 and 75°C but has an optimum temperature of $\sim 30^\circ\text{C}$. Soil temperature affects not only the rate of microbial metabolism, but also influences chemical processes such as the rate of diffusion of O_2 , NO_3^- , N_2O , and N_2 in the soil water and soil atmosphere. The optimum pH range for denitrifying organisms is from 6.0 to 8.0, but as with nitrification, denitrification has also been measured in highly acidic soils. Estimates of the amount of N lost from soils by denitrification vary from 5 to 15 kg N/ha/year for well-drained soils to as much as 60 kg N/ha/year for poorly drained, high-organic-matter soils. Denitrification can also occur in streams, rivers, and groundwaters.

Because NO_3^- originates primarily by nitrification, an aerobic process, the soil conditions most conducive to denitrification are alternating aerobic and anaerobic cycles or adjacent aerobic and anaerobic zones. Soils that are periodically flooded or experience transitory anaerobic conditions due to heavy rains can accumulate pools of NO_3^- in an aerobic period that is later lost by denitrification during an anaerobic cycle. Rapid O_2 consumption by soil microorganisms during decomposition of organic matter can produce anaerobic zones adjacent to aerobic areas where NO_3^- is being produced. When NO_3^- moves into the anaerobic zone by diffusion or mass flow, it can then be denitrified, as shown in Figure 5.16 for a soil receiving slit injections of a pharmaceutical by-product. Common examples of anaerobic zones are microsites in the rhizosphere that have been enriched with root exudates, localized deposits of highly decomposable crop residues, and organic by-products injected into relatively small soil volumes, as opposed to a more uniform spatial distribution. An ecological example would be a wetland adjacent to an agricultural field or perhaps an artificial wetland used to treat wastewaters from a livestock operation (Figure 5.17). In these

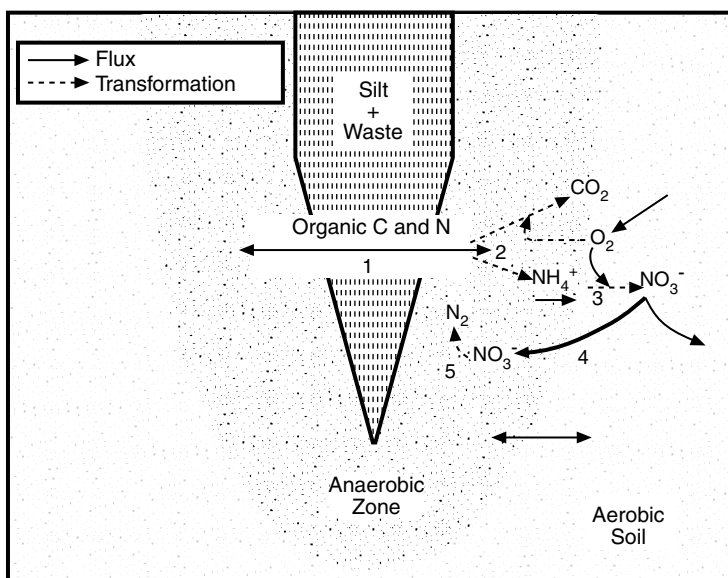


Figure 5.16 Denitrification induced by slit injection of a highly decomposable pharmaceutical by-product. Concentrating available C stimulates high O_2 consumption, producing an anaerobic zone adjacent to an aerobic zone where nitrification occurs as by-product mineralizes. (From Rice, C. W. et al., *Soil Sci. Soc. Am. J.*, 52, 102–108, 1988. With permission.)

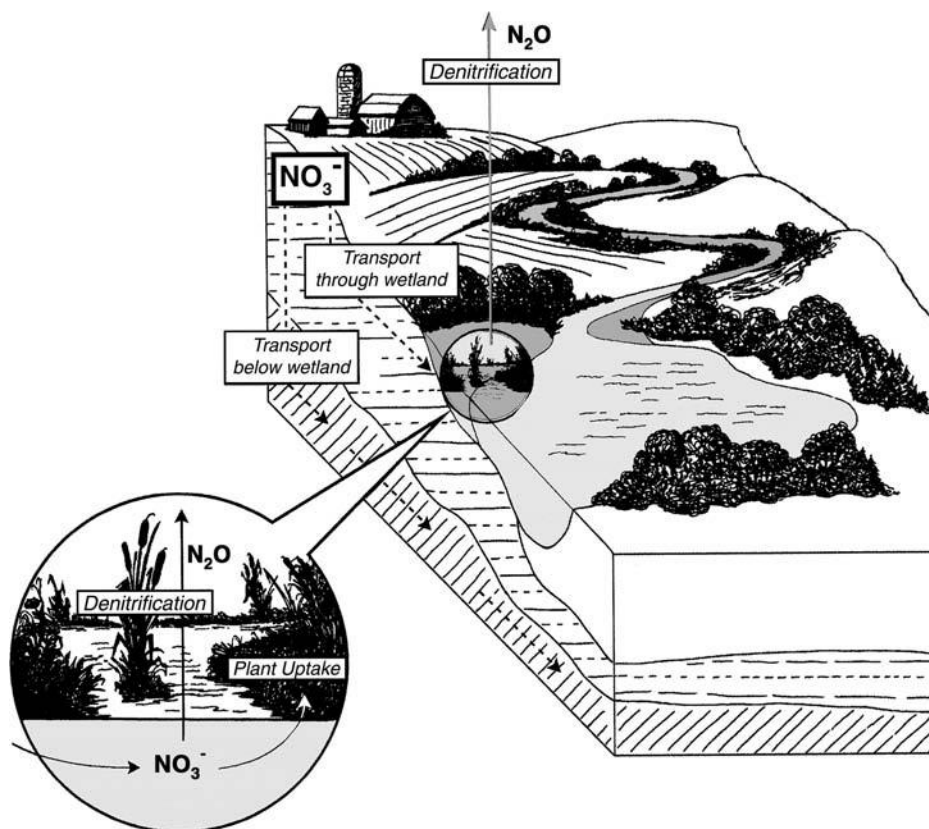


Figure 5.17 Wetlands as denitrifying zones capable of removing NO_3^- from runoff or subsurface drainage from agricultural fields.

situations NO_3^- produced in the normally aerobic field soil moves by leaching and lateral flow into the wetland, dominated by flooded anaerobic conditions and high quantities of available C, and is then removed from drainage waters by denitrification. Riparian buffers located between agricultural fields and streams or rivers can also function as denitrifying zones, as seen in Figure 5.18 for a small stream in Oregon (U.S.A.) that receives NO_3^- from adjacent agricultural fields used for commercial production of grass seed. Buffer effectiveness at NO_3^- removal can vary as a function of site hydrology, buffer dimensions, vegetation, and soil geochemistry. In this study, a noncultivated riparian zone (NCR) decreased NO_3^- concentrations entering Lake Creek more than a cultivated riparian zone (CR). The NCR was wider (30 to 48 m), composed of a more diverse vegetative community (grasses, forbs, sedges, rushes), had higher levels of soil C, and maintained a lower redox potential than the CR (10 to 15 m wide, mix of a few grass species).

As is true of NH_3 volatilization, denitrification has both economic and environmental costs. Conversion of NO_3^- to NO , N_2O , or N_2 represents the loss of a valuable plant nutrient from soils and the release of reactive N oxides to the atmosphere where they can contribute to ozone destruction, leading to increased human exposure to ultraviolet radiations and more incidences of skin cancer. Research has also shown that N oxides are several hundred times more effective than CO_2 in absorbing infrared radiation emitted from the Earth's surface and thus may play a major role in the greenhouse effect and global warming.

In some cases, particularly where organic N sources are surface-applied, there is a need to understand and control the gaseous losses of both NH_3 and NO_x . A New Zealand study of the effects of pig slurry application to a ryegrass–clover pasture illustrates the rather complex nature of gaseous N evolution from manured soils (Figure 5.19). The slurry was an alkaline material rich

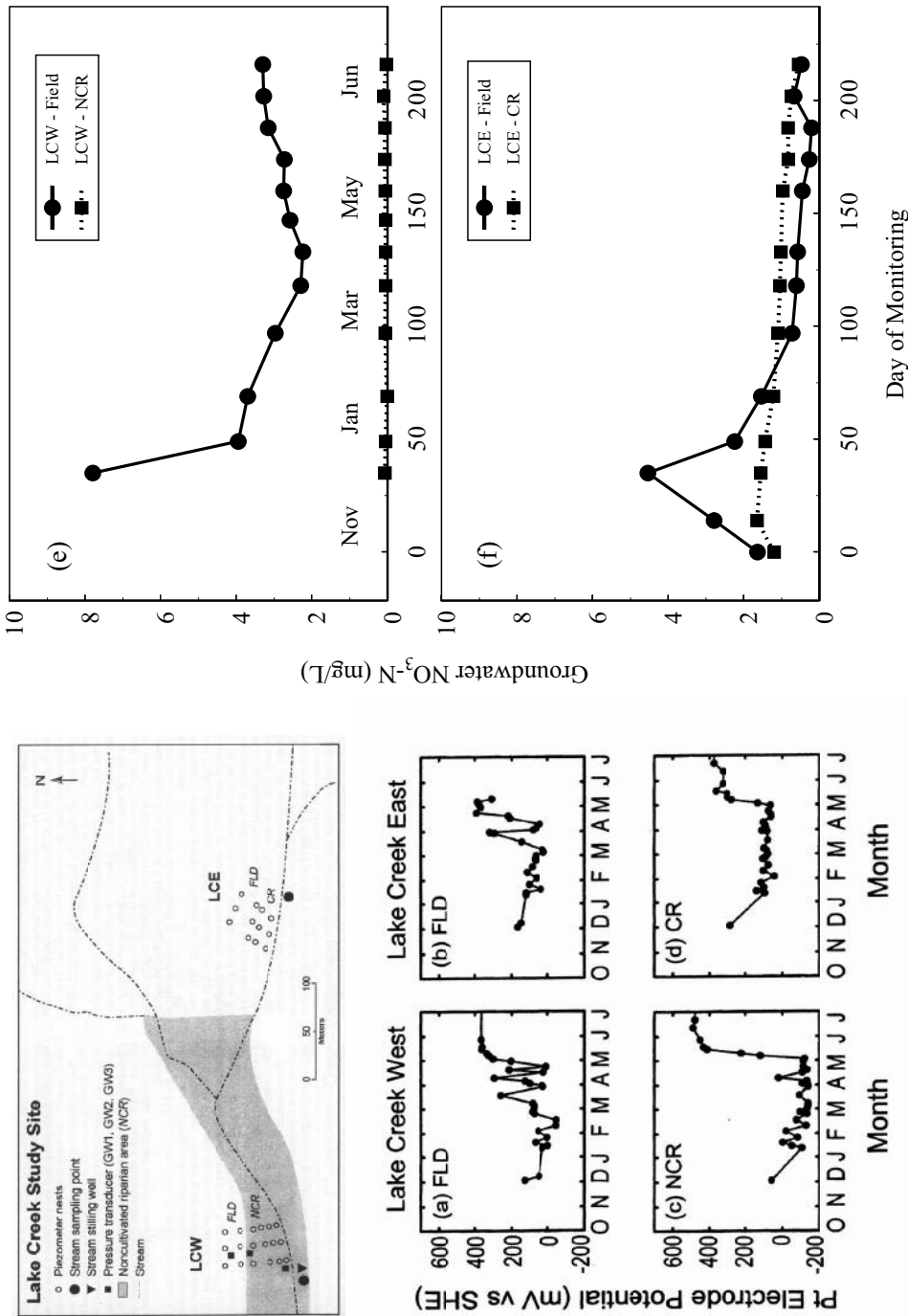


Figure 5.18 Effects of riparian buffer type (noncultivated = NCR vs. cultivated = CR) and (a–d) soil geochemistry, as indicated by redox potential, on (e, f) $\text{NO}_3\text{-N}$ concentrations in the shallow groundwater discharging from two agricultural fields into a small creek in Oregon. (From Wignington, P. J. et al., *J. Environ. Qual.*, 32, 162–170, 2003. With permission.)

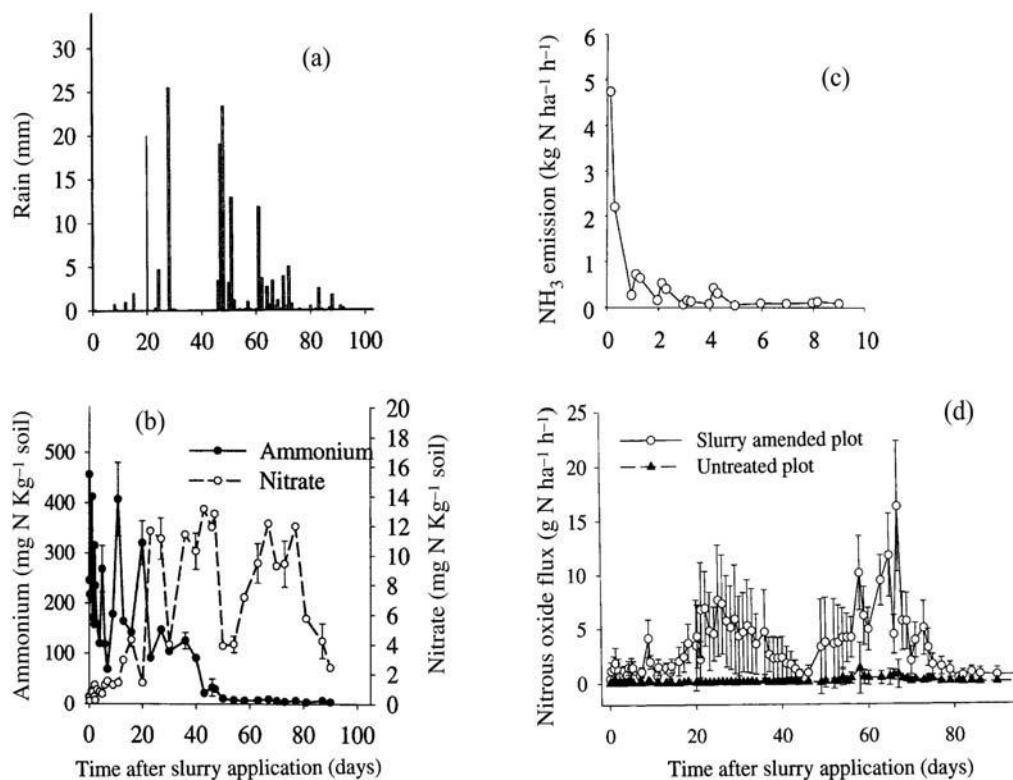


Figure 5.19 Relationship between (a) rainfall patterns and (b) soil ammonium-N and nitrate-N transformations on (c) NH_3 volatilization and (d) nitrous oxide emissions from a New Zealand pasture receiving surface applications of pig slurry. (From Sherlock, R. R. et al., *J. Environ. Qual.*, 31, 1491–1501, 2002. With permission.)

in NH_3 and available C. Rainfall patterns after slurry application and soil inorganic N changes are shown in Figure 5.19a and b. Immediately after slurry was applied, soil NH_4^+ concentrations increased markedly and NH_3 began to volatilize from the pasture (Figure 5.19c). Volatilization decreased rapidly and within less than a week had returned to background levels. Possible causes for this were the formation of a crust on the slurry that inhibited NH_3 diffusion into the atmosphere, leaching of liquid slurry into the soil and adsorption of NH_4^+ on soil cation exchange sites, onset of nitrification, which converted NH_4^+ into NO_3^- , and rainfall that could have leached some of the NH_4^+ into the pasture soil. Denitrification, as indicated by N_2O evolution, occurred throughout the study (Figure 5.19d). However, denitrification losses increased as NO_3^- built up in soils and peaked shortly after rainfall events (e.g., days 20, 40, and 60) that, together with consumption of O_2 by microbial decomposition of slurry organic C, would have promoted anaerobic conditions in pasture soils. Field studies such as these help to quantify the potential for N loss and also identify the conditions that create the greatest losses. Using this knowledge, we seek to develop N management practices that can minimize N losses to the atmosphere.

5.2.3 Leaching and Erosional Losses of Nitrogen

Nitrogen can be transported from soils into groundwaters and surface waters by leaching, erosion, or runoff. Losses of N by leaching occur mainly as NO_3^- because of the low capacity of most soils to retain this anion. In general, any downward movement of water through the soil profile will cause the leaching of NO_3^- , with the magnitude of the N loss proportional to the concentration

of NO_3^- in the soil solution and the volume of leaching water. Leaching of NO_3^- is economically and environmentally undesirable. Nitrate that leaches below the crop rooting zone represents the loss of a valuable plant nutrient, and, as mentioned earlier, can contribute to pollution of groundwater aquifers and eutrophication of surface waters, as shown in Figure 5.20. Much of the research conducted with fertilizers, animal manures, and other by-products (e.g., biosolids) has been directed toward reducing NO_3^- leaching, especially in humid regions. Controlling N leaching is very problematic, given the need to produce food and fiber for a growing world population and to use agricultural by-products, such as manures, beneficially.

A 3-year Pennsylvania field study used large zero-tension pan lysimeters to measure NO_3^- leaching from an inorganic N fertilizer (NH_4NO_3) applied to nonmanured (NM) and manured (M) soils used for corn production (Figure 5.21). The goal was to determine if corn could be economically produced without creating leachate that exceeded the EPA drinking water standard (10 mg $\text{NO}_3\text{-N/L}$). Results showed that broadcasting of N fertilizer at the time of corn planting resulted in flow-weighted annual concentrations in leachate of about 18 to 20 mg $\text{NO}_3\text{-N/L}$ at the economically optimum N rate (EON). Using manure alone, without supplemental N fertilizer (0_M treatment) also caused leachate to exceed the EPA standard. The mass of NO_3^- leached below the crop rooting zone of fertilized and manured soils was from 50 to 110 kg $\text{NO}_3\text{-N/ha}$ and recovery of applied fertilizer N ranged from 19 to 44%. Clearly, a more efficient approach to fertilizer and manure N management would be required to produce corn without negatively affecting groundwater quality. Numerous examples of best management practices (BMPs) that can be implemented to improve N use efficiency are provided in Chapter 8.

Nitrate pollution of groundwaters, however, is not a universal problem and is often regional or local in nature, as shown in Color Figure 5.4. Situations most conducive to NO_3^- leaching and groundwater pollution include sandy, well-drained soils with shallow water tables in areas that receive high rainfall or intensive irrigation and frequent use of fertilizers, manures, or other N sources. Nitrate leaching concerns are not restricted to these conditions, however. Any situation

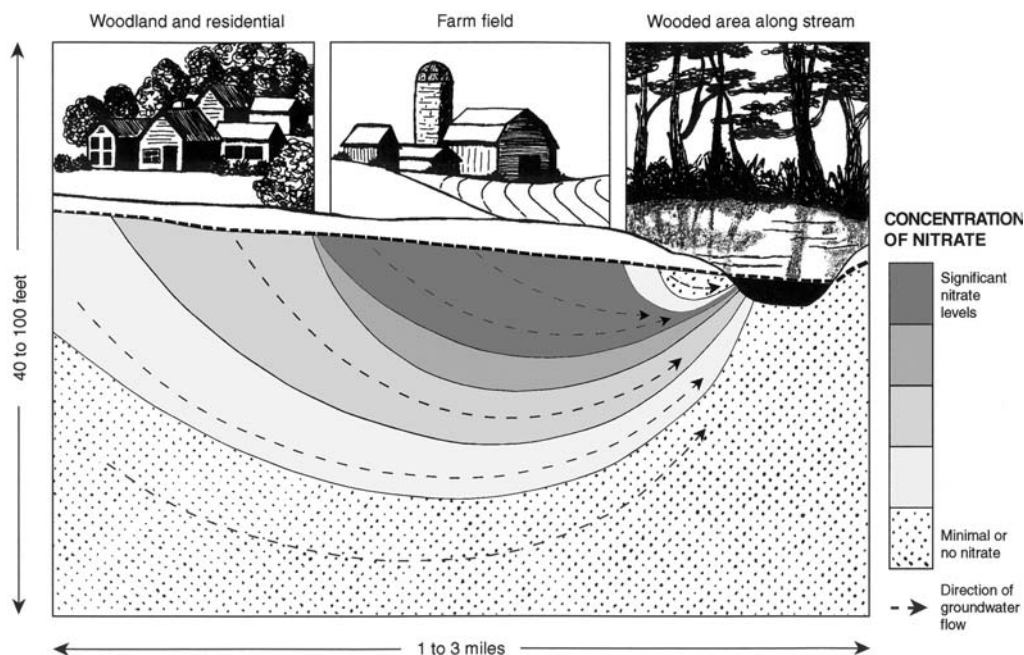


Figure 5.20 Generalized representation of NO_3^- transport in groundwater aquifers, illustrating variable nature of NO_3^- concentration with land use, aquifer depth and distance to discharge area. (Adapted from Hamilton and Shedlock, 1992.)

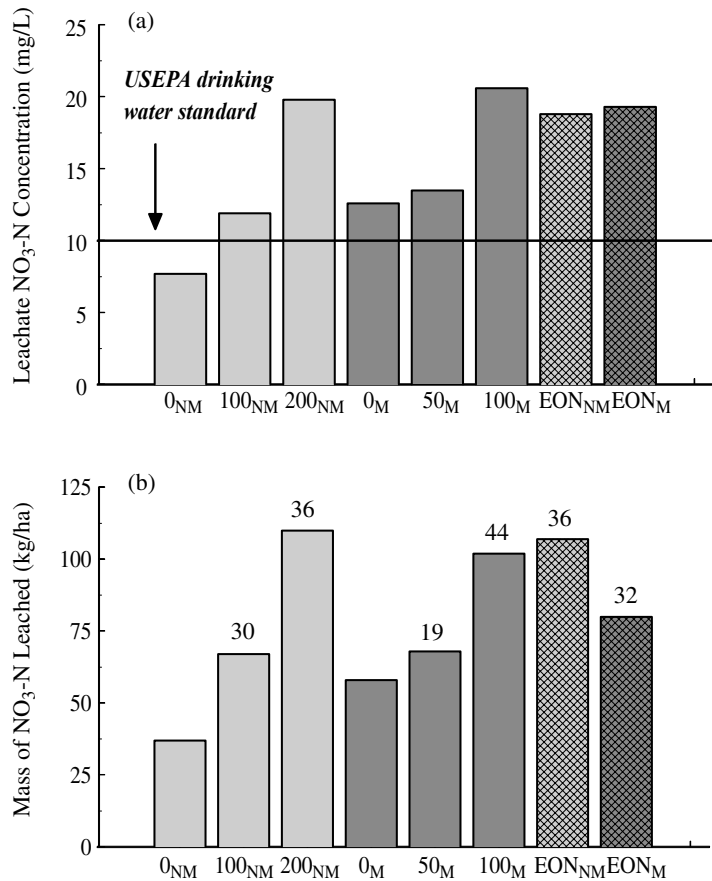


Figure 5.21 Influence of fertilizer N rate (kg N/ha) on NO_3^- leaching from nonmanured (NM) and manured (M; dairy manure) corn grown on a silt loam soil (Typic Hapludalf) in Pennsylvania: (a) 3-year average NO_3^- concentrations in leachate from large pan lysimeters; (b) mass of NO_3^- leached (kg N/ha; values above bars are percentages of added fertilizer N that was leached below root zone of crop). EON is the economically optimum N rate which was 192 kg N/ha for NM and 66 kg/ha for M corn. (From Jemison, J. M. and R. H. Fox, *J. Environ. Qual.*, 23, 337–343, 1994. With permission.)

involving overapplication of N, organic by-product storage areas (e.g., feedlots, lagoons), or intensive irrigation has the potential to cause significant NO_3^- leaching, regardless of soil type and climate. Chemical retention of NO_3^- in soil profiles, unlike other anions (phosphate, sulfate) is generally of little value in reducing leaching, although some highly acidic subsoils have been shown to have significant anion exchange capacity (AEC). This is clearly seen in Figure 5.22a, which shows how decreasing pH increased NO_3^- -N adsorption by the subsoil horizon of an Ultisol from Georgia (U.S.A.). In the same experiment, column leaching studies with 16 subsoil horizons from the southeastern United States and several tropical countries showed the retardation coefficient for NO_3^- leaching increased linearly with subsoil AEC (Figure 5.22B). The development of positively charged sites on the surfaces of variably charged clays in these soils under acid conditions thus can act to prevent leaching losses of NO_3^- to groundwaters.

Denitrification in groundwaters or groundwater discharge areas (e.g., wetlands) may reduce the environmental impacts of NO_3^- leaching, ideally by complete conversion of NO_3^- to the inert, unreactive gaseous form, N_2 . Subsoil denitrification, however, is less likely to be of value in mitigating NO_3^- leaching, primarily because of the low available C levels in most subsoils. Some of the factors affecting subsoil denitrification are shown in Figure 5.23. This 4-year field study

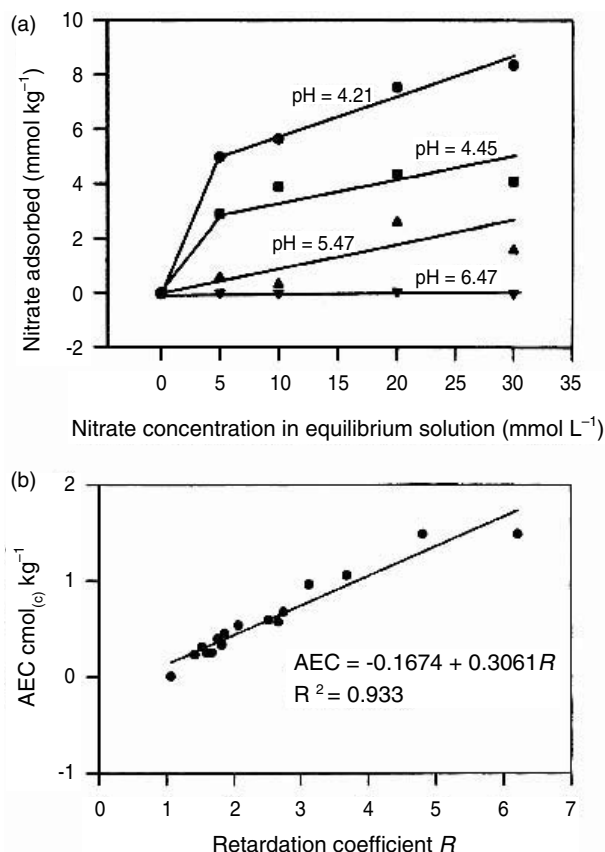


Figure 5.22 Effect of (a) soil pH on NO_3^- adsorption by the subsoil of an Ultisol from the southeastern United States, and (b) anion exchange capacity of 16 subtropical and tropical soils on the retardation coefficient for NO_3^- leaching. (From Qafoku, N. P. et al., *J. Environ. Qual.*, 29, 484–493, 2000. With permission.)

used lysimeters to measure the leaching of NO_3^- and dissolved organic C (DOC) from corn grown in a silt loam soil using two different conservation tillage practices (no-till, chisel plow). Potentially denitrifiable NO_3^- (PDN) in subsoils at a depth of 1.4 m was calculated from the concentrations of NO_3^- and DOC in leachate, assuming that all DOC was available for denitrifying bacteria and that conditions in subsoils were optimum (e.g., very low O_2) for denitrification. Most NO_3^- leaching in this study occurred between January and June during periods of snowmelt, spring rains, and crop fertilization. Results showed that subsoil denitrification could occur, particularly during winter and early spring when wetter soil conditions were conducive to NO_3^- reduction. High PDN values in midsummer reflect the leaching of NO_3^- applied to corn in the spring; denitrification would only occur at this time of year if subsoils became saturated by summer rainfalls. Denitrification was predicted to be higher for chisel-plowed soils, which consistently had higher subsoil DOC values and more water draining to subsoils, than no-tilled soils (Figure 5.23a). The amounts of PDN were 9 to 34% of total NO_3^- leached, ranging from 8 to 10 kg N/ha/year, compared to average annual NO_3^- leaching losses of 40 to 50 kg N/ha/year (Figure 5.23b). The main factor limiting denitrification was the amount of DOC present in subsoils, not the amount of substrate (NO_3^-).

In any case, given the atmospheric impacts of N oxides, management techniques designed to control leaching by enhancing denitrification are certain to be examined more carefully in the future. Approaches to minimize NO_3^- leaching, therefore, are operational in nature and focus on controlling the timing of NO_3^- formation in soils, understanding the soil and climatic conditions of the region,

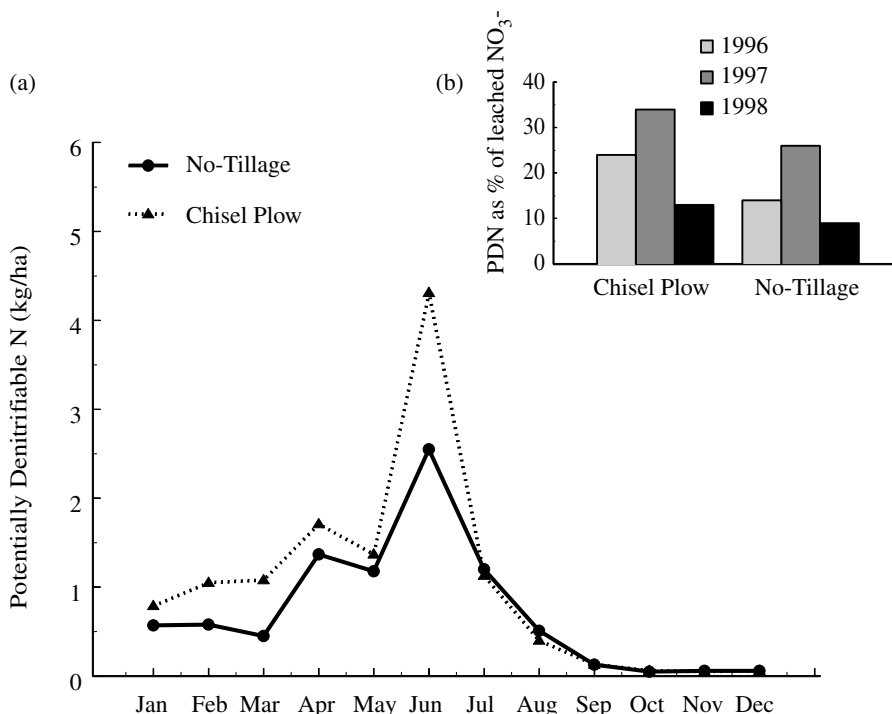


Figure 5.23 Lysimeter study of the effect of no-tillage or chisel-plow cultivation of corn in Wisconsin on seasonal trends for (a) the amount of potentially denitrifiable NO_3^- (PDN) that leached to a depth of 1.4 m in a silt loam soil (Typic Argiudoll); and (b) the percentage of the total amount of NO_3^- leached that was potentially denitrifiable. Values for PDN were calculated assuming all dissolved organic carbon that leached from the lysimeters was available for denitrifying microorganisms and that other conditions in subsoils (e.g., extremely low O_2 concentrations) were conducive to denitrification. (From Brye, K. R. et al., *J. Environ. Qual.*, 30, 58–70, 2001. With permission.)

and developing an appreciation for N uptake patterns of the dominant vegetation or crops produced. These approaches, their implications, and constraints are discussed in more detail in Chapter 8.

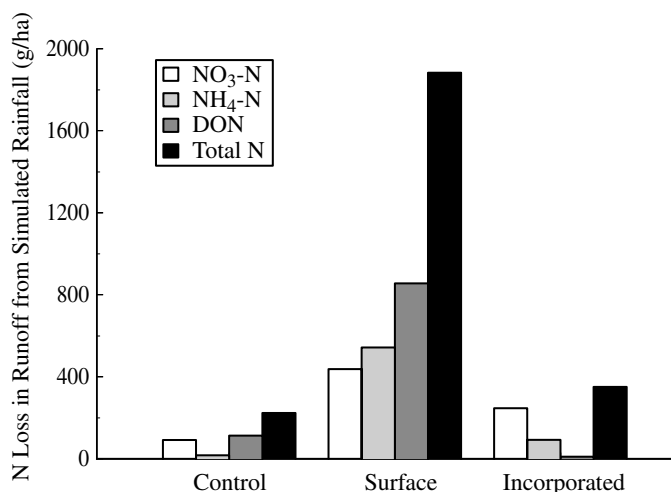
Erosion refers to the transport of soil from a field by water or wind; *surface runoff* is the water lost from a field when the rate of precipitation or irrigation exceeds the infiltration capacity of the soil. Both processes can transport particulate N and dissolved inorganic and organic N to surface waters and contribute to the process of eutrophication or drinking water contamination. Many watershed studies have shown that most of the N lost by erosion or runoff is sediment-bound organic N. Although the solubility of NO_3^- favors its loss in runoff as opposed to sediment transport, total N losses from most watershed studies are usually severalfold greater than soluble N. Exceptions include grasslands and other settings where sediment loss is very low; in such cases NO_3^- and dissolved organic N (DON) can make up an appreciable amount of total N lost in surface flow.

Surface applications of organic by-products are undesirable because they increase the likelihood of dissolved inorganic and organic N losses by erosion and runoff. This approach is usually not permitted with municipal and industrial by-products, but in agricultural operations, conservation practices designed to control erosion by reducing tillage often result in application of animal manures to soil surfaces. Surface applications of manures can also occur when farmers apply manures during winter months, when the soil is frozen and less susceptible to equipment damage and erosion, and more time is available. The use of grassed waterways or border strips that trap sediment and accumulate soluble N in plant biomass can help reduce N losses in these situations, as shown in Table 5.4 where a cornstalk residue strip 2.7 m wide with 50% ground cover reduced sediment and total N losses by 70 to 80%. In grassland settings, new equipment has been developed

Table 5.4 Influence of Antecedent Soil Moisture Conditions on the Effectiveness of Residue Strips at Reducing Erosion and Runoff Losses of Nitrogen from a Bare Soil with 5% Slope

Strip Width, Residue Cover, and Antecedent Moisture	Entering Residue Strip			Leaving Residue Strip		
	Sediment	Runoff	Total N	Sediment	Runoff	Total N
	—kg/h/m of width—		g/h/m of width	—kg/h/m of width—		g/h/m of width
1.8 m and 27% Cover						
Dry	9.5	171	22.5	6.0	244	16.5
Very wet	16.6	320	31.9	14.3	373	28.2
2.7 m and 50% Cover						
Dry	22.7	284	45.3	4.9	280	14.1
Very wet	24.0	386	39.4	4.9	462	13.0

Adapted from Alberts et al., 1981.

**Figure 5.24** Effect of incorporating poultry litter into perennial grassland soils on N losses in runoff, as estimated by a rainfall simulation method. Dissolved organic N (DON) calculated as the difference between total N and (NH₄-N + NO₃-N). (From Pote, D. H. et al., *J. Environ. Qual.*, 32, 2392–2398, 2003. With permission.)

that can inject liquid and solid manures into pastures without damaging the vegetation. This can decrease N losses to surface waters, as shown in Figure 5.24 in a study from Arkansas (U.S.A.) where incorporating poultry litter into a tall fescue pasture reduced the loss of all forms of N in surface runoff. This study also showed that “knifing” litter into the pasture increased fescue yields and infiltration of rainfall and decreased the volume of runoff water lost, factors that improve the agronomic and environmental efficiency of manure use on grasslands.

5.2.4 Biological Nitrogen Fixation

Biological N fixation is the conversion of atmospheric N₂ into an organic form of N, either through symbiotic associations between plants and microorganisms, or independently by free-living organisms such as cyanobacteria (blue-green algae) and certain heterotrophic bacteria. In the context

of the global N cycle, biological N fixation represents the major N input to soils. It has been estimated that from 100 million to 150 million Mg of N are fixed each year by terrestrial biological processes. In contrast, the total amount of N produced by the world fertilizer industry is about 75 million to 80 million Mg/year. Integrating biological N fixation into agro-ecosystems is of considerable value to the world economy and environment. Doing so reduces the energy-intensive production of N fertilizers and also provides a means to improve N nutrition of plants grown in areas that cannot be fertilized because of logistical or economic limitations. Advantages such as these have stimulated considerable interest in the genetic engineering of major food crops incapable of N fixation (e.g., corn, rice, wheat) to incorporate the genes needed for this valuable biological process.

Symbiotic N fixation can occur between leguminous plants and bacteria, nonlegumes and actinomycetes, and plant–algal associations. In this symbiosis an N-fixing organism can enzymatically reduce N_2 to NH_3 using an energy supply (photosynthate) provided by the host. From an agricultural perspective, the most important symbiotic N fixation is that occurring between leguminous plants and bacteria of the genera *Rhizobium* and *Bradyrhizobium*. Leguminous plants have been important components of agricultural crop production systems for centuries and represent a major pathway for the conversion of atmospheric N_2 to soil N and then to a form that can be used by humans and animals. More than 14,000 species of legumes are known, of which more than 100 are commonly used in agriculture. In addition to their value as food crops, some legumes are grown as cover crops to provide N for a subsequent nonlegumes (e.g., clovers or vetches followed by corn). Legumes are also often seeded together with nonlegumes (e.g., grass–legume pastures). Nitrogen fixed by the legumes is released throughout the growing season by mineralization of root exudates, root debris, and aboveground plant residues; this N is then taken up by the nonlegumes, reducing the need for N fertilization.

Although we focus below mainly on the process and management of N fixation by legumes, it should be recognized that the ability of nonlegumes to fix atmospheric N_2 can be equally important to nonagricultural ecosystems and to certain crops. More than 200 species of nonleguminous plants have been shown to be capable of biological N fixation. An example of nonleguminous N fixation is the symbiotic relationship between actinomycetes of the genus *Frankia* and a wide variety of trees and woody shrubs that are important in soil formation, revegetation of disturbed, highly erodible forest soils, and as sources of fuel wood. A nonleguminous, agricultural example of symbiotic N fixation is the association between the cyanobacterium *Anabaena* and the freshwater, free-floating fern *Azolla* found widely in flooded, tropical areas used for rice production. The *Anabaena* are located on the stem and fronds of *Azolla*, but unlike *Rhizobium* or *Frankia*, they do not directly convert N_2 into organic N within the plant. Rather, *Anabaena* produce soluble NH_4^+ that is taken up by *Azolla* roots growing in the water or upper portion of the sediment of a rice paddy. This fixed N can then be used directly by rice when the *Azolla* die and the organic N is mineralized, or in some countries, the *Azolla* is harvested and used as animal feed or an organic fertilizer.

The biochemical mechanisms of N fixation have been studied extensively and are thus well known. For legumes, symbiotic N fixation begins when bacteria living in the soil near the root system of a host plant attach themselves to cells of root hairs and in doing so induce a curling of the root hair around the bacteria. The bacteria then produce an infection thread that invades the root cell, allowing bacterial penetration and proliferation within the root cortex. In response to this bacterial invasion, the plant synthesizes a nodule, a protective structure that encapsulates the bacteria that have now changed both physical shape and metabolic function and that are now referred to as bacteroids (Figure 5.25). The bacteria–host plant relationship is often quite specific and a given species of *Rhizobium* or *Bradyrhizobium* will not infect or nodulate incompatible host plants. The nodule is comparable to other energy-converting organs in the plant, and possesses a membrane that regulates the entry and exit of metabolites to and from the bacteroids. In the N fixation reaction bacteroids use photosynthate-derived energy (ATP and electrons), O_2 , and a specific enzyme, *nitrogenase*, to reduce N_2 to NH_4^+ , which is released into the host cell and used in the synthesis of amino acids and proteins. The overall equation for symbiotic N fixation is



Each host plant–bacteria association has its own genetic potential for N fixation. For a given symbiosis, the actual amount of N fixed depends primarily on available soil N and the energy status of the plant, which, in turn, is influenced by such factors as carbohydrate supply, light intensity, soil nutrient status, soil temperature, and moisture. Examples of agriculturally important legumes and estimated amounts of N fixed under optimum conditions are given in Table 5.5.

A generalization of environmental factors important in N fixation would include soil pH (near neutral), an adequate supply of key nutrients (P, K, Ca, Cu, Fe, Mo, Co), “optimum” temperature and moisture (varies with host plant), adequate aeration, and a low level of available soil N (NH_4^+ and NO_3^-). It is important to remember, however, that even under optimum conditions legumes

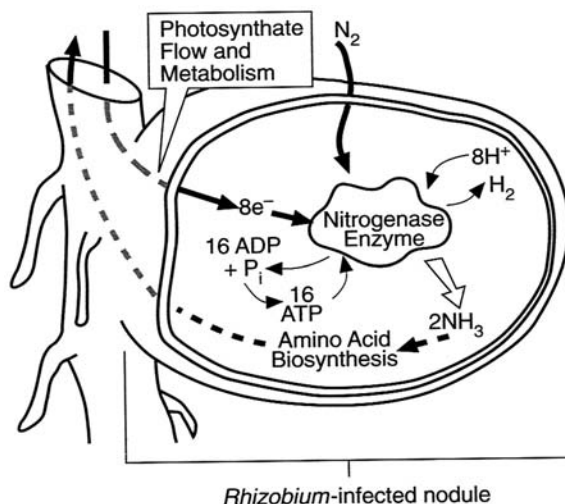


Figure 5.25 Schematic representation of the form and function of bacteroids in the nodules of legume roots.

Table 5.5 Major Legume Crops Used in Agriculture and Estimates of Annual N Fixation

Crop and N-Fixing Bacteria		Annual N_2 Fixation	
		Range	Typical Value
—kg N/ha/yr—			
Host Plant	<i>Rhizobium</i>		
Alfalfa	<i>R. meliloti</i>	60–500	225
Clovers	<i>R. trifolii</i>	60–350	115
Peas, vetch	<i>R. leguminosarum</i>	90–180	100
Beans	<i>R. phaseoli</i>	20–100	45
Host Plant	<i>Bradyrhizobium</i>		
Lupins	<i>B. lupinii</i>	150–170	160
Soybeans	<i>B. japonicum</i>	65–200	100
Cowpea	<i>B. parasponiae</i>	65–130	100

Note: *Rhizobium* are fast-growing symbiotic bacteria; *Bradyrhizobium* are slow-growing. Average values from various sources.

do not obtain all their N from biological N fixation. Soil N can provide as much as 50% of the total N in legumes with low fixation rates. Also, if the soil solution concentration of NO_3^- exceeds $\sim 1 \text{ mM}$ ($\sim 62 \text{ mg/L}$), the process of N fixation is restricted. This can occur when legumes are planted in soils with high levels of residual N, perhaps resulting from previous fertilizer or organic by-product applications. If supplied with sufficient N fertilizer, legumes will not nodulate and N fixation will not occur. This has led to debates over the economic value of “starter” N fertilizers for legumes (e.g., soybeans) as well as the environmental impact of applying organic N sources, such as manure and biosolids, to legumes. The presence of a small amount of available N prior to effective nodulation may benefit the plant, but excessive fertilizer N will often reduce or prevent biological N fixation.

In addition to symbiotic processes, N fixation can occur with some species of “free-living” organisms. The major examples are the cyanobacteria (e.g., *Anabaena*, see above) that are autotrophic (requiring only light, water, N_2 , CO_2 , and salts) and certain heterotrophic bacteria. Important nonsymbiotic, N-fixing bacteria include *Azotobacter* and *Beijerinckia*, aerobic saprophytes that obtain their energy from the oxidation of organic matter; *Azospirillum*, facultatively anaerobic bacteria; and *Clostridium*, anaerobic saprophytes. In general, because the amount of N fixed by these bacteria is small (5 to 50 kg N/ha), the bacteria are of little importance to most soil N management programs.

5.2.5 Nitrogen Additions to Soils

The production of food and fiber, the growth of plants for aesthetic purposes, and the reclamation and stabilization of lands disturbed by construction, mining, and other industrial or urban activities often require the addition of supplemental N to obtain optimum plant growth. Two broad categories of N sources exist: inorganic and organic. Inorganic N sources are predominantly commercial fertilizers, but also include limited quantities of mineral deposits and industrial by-products. Organic N sources commonly include animal manures, crop residues, municipal biosolids and wastewaters, and a wide variety of industrial organic by-products.

For most of recorded history, the major source of N added to soils was organic in nature, primarily as animal manures or crop residues. The first N fertilizer used commercially in the United States, Peruvian guano, was also organic in nature, formed from centuries of deposition of excreta by seafowl along the South American coast. In the late 1800s and early 1900s, industrial processes were devised that could fix atmospheric N_2 , converting it to either NH_3 gas, calcium cyanamide (CaCN_2), or nitric acid (HNO_3). Later improvements in the efficiency of one such process, the Haber–Bosch method for synthesis of NH_3 gas from atmospheric N_2 , resulted in the availability of inexpensive, high analysis N fertilizer materials, which began to markedly change the nature of agriculture on a global scale. Food production was no longer limited by the availability of soil, manure, or legume N because fertilizer N could now be used to increase yields of most agricultural crops greatly. Beyond this, the ease of handling commercial N fertilizers reduced labor requirements of crop production and contributed to the development of larger, more specialized farms devoted in many cases to the production of fewer crops.

Global trends in N fertilizer production for the past 40 years are shown in Figure 5.26a. Since 1960, the world capacity to produce N fertilizer has grown nearly tenfold, particularly in Asia, Europe, and North America. In fact, today, Asia clearly dominates the world fertilizer N production market. The types of N fertilizer produced have also changed in the past 30 years. Urea, an inexpensive, high-N-content fertilizer, mainly produced in Asia and the former U.S.S.R., now dominates global N fertilizer consumption (Figure 5.26b). Understanding the nature of fertilizer N trends is important because these changes dictate the forms of N that will be added to world soils and thus the types of transformations and N losses that can occur. For example, as was discussed earlier, urea is particularly susceptible to N losses by volatilization; hence the atmospheric impacts of N fertilizer use are likely to become an even greater concern in the future.

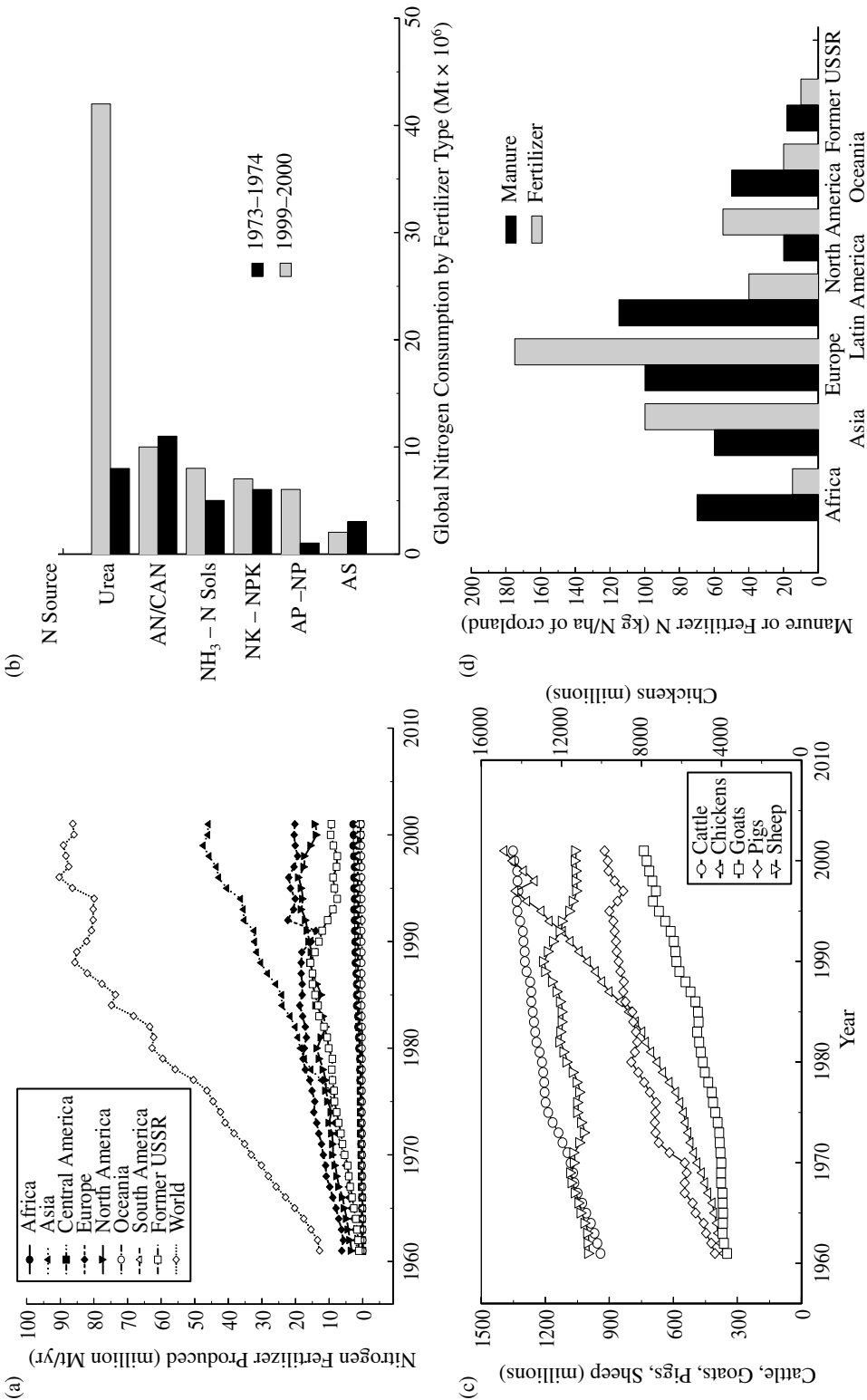


Figure 5.26 Global trends in N source production and consumption: (a) total N fertilizer production by major world region; (b) changes in major fertilizer N sources consumed from 1973 to 2000; (c) number of livestock produced worldwide, by species; and (d) amount of manure and fertilizer N available for land application in major world regions (1999). (From Burkart and Stoner, 2001; FAO, 2004; IFA, 2004.)

Increased fertilizer N production capacity has not always equated to increased efficiency of N use. As farmers, and those advising farmers, learned to use new fertilizer materials alone or in combination with organic N sources, new application equipment, and new cropping systems, they often proceeded without a real understanding of the potential environmental impacts involved. The uncertainty associated with these new production practices and the low costs of fertilizer N undoubtedly resulted in overfertilization with N and contributed to groundwater contamination by NO_3^- , especially in areas of intense fertilizer use.

Changes have also occurred in the amount and geographic distribution of organic N sources produced in the world. As seen in Figure 5.26c, the global livestock population has also grown dramatically since 1960, particularly the world production of chickens. Associated with the increase in animal numbers has been an increase in the amount of manure that must be applied to cropland. The nature of modern animal production has resulted in an uneven geographic distribution of manure in the world, with the largest amounts of manure N produced today in Europe and Latin America (Figure 5.26d). Areas of greatest fertilizer N production (Asia, Europe, and North America) use more fertilizer N than manure N. However, as seen in Figure 5.9a, the modern, geographically concentrated nature of animal production often results in localized excesses of manure N within countries that rely mainly on fertilizer N (e.g., the United States), creating formidable environmental problems.

Regardless of the form of N used or the nature of the soil–plant system, maximizing the efficiency of N recovery and minimizing the potential of the N source to pollute the environment are now fundamental goals of modern agriculture. To manage either type of N source properly, it is essential to understand how the physical, chemical, or biological properties of the material affect its handling, application, and fate among the many transformations of the soil N cycle. It is also important to understand that all environmental problems associated with improper N management can be caused by both inorganic and organic N sources. That is, despite the interest in sustainable agriculture and organic farming, research has found no intrinsic superiority associated with organic N sources. In fact, in many situations, the physical properties and heterogeneity in composition of organic by-products make them more difficult to manage successfully than inorganic N fertilizers.

The purpose of the following sections is to provide an overview of the production, composition, and characteristics of major inorganic and organic sources of N. The principles and BMPs used to manage N in agricultural and nonagricultural settings are discussed in Chapter 8 (Nutrient Management Planning).

5.2.5.1 Inorganic Sources of Nitrogen

Most commonly used N fertilizers, summarized in Table 5.6, are produced from NH_3 gas synthesized by the Haber–Bosch process. This process uses natural gas (CH_4), atmospheric N_2 , and steam (H_2O) to produce NH_3 gas as follows:



This clearly illustrates another environmental aspect of N use, its impact on natural resources, as the production of N fertilizers consumes natural gas, a finite and critically important natural resource. Efficient use of N fertilizers will thus enhance the longevity of natural gas supplies.

Once NH_3 has been synthesized, it can be (1) used directly as anhydrous ammonia, a pressurized gas, NH_3 ; (2) reacted with CO_2 to form urea, $\text{CO}(\text{NH}_2)_2$; (3) oxidized to NO_3 and reacted with more NH_3 to form ammonium nitrate, NH_4NO_3 ; and (4) combined with sulfuric acid to produce ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, or with various types of phosphoric acid to form ammonium phosphates such as diammonium phosphate (DAP), $(\text{NH}_4)_2\text{HPO}_4$, or monoammonium phosphate (MAP), $\text{NH}_4\text{H}_2\text{PO}_4$. Further industrial processes can produce N solutions such as urea-ammonium-nitrate (UAN) or aqua

Table 5.6 Properties of Major Commercial N Fertilizers

Nitrogen Source	Chemical Composition	%N
Ammoniacal N Sources		
Anhydrous ammonia	NH_3	82
Aqua ammonia	$\text{NH}_3 \cdot \text{H}_2\text{O}$	20–25
Ammonium chloride	NH_4Cl	25
Ammonium nitrate	NH_4NO_3	33
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	21
Nitrate N Sources		
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	15
Potassium nitrate	KNO_3	13
Sodium nitrate	NaNO_3	16
Urea Materials		
Urea	$\text{CO}(\text{NH}_2)_2$	45
Urea-ammonium-nitrate solutions	30–35% urea: 40–43% NH_4NO_3	28–32
Ureaform	Urea-formaldehyde	38
IBDU	Isobutylidene diurea	32
SCU	S-coated urea	36–38
Nitrogen–Phosphorus Materials		
Monoammonium phosphate (MAP)	$\text{NH}_4\text{H}_2\text{PO}_4$	11
Diammonium phosphate (DAP)	$(\text{NH}_4)_2\text{HPO}_4$	18–21
Ammonium polyphosphates (liquid)	$(\text{NH}_4)_3\text{HP}_2\text{O}_7$	10–11

ammonia (NH_3), or controlled, slow-release, solid N fertilizers that are coated with resins (Osmocote, used in greenhouses and nurseries) or sulfur (S-coated urea) to delay their rate of dissolution in the soil. A wide variety of mixed fertilizers containing N, P, K, and other nutrients are also produced. Many urban situations (e.g., turf, home gardens) and land reclamation projects make extensive use of mixed fertilizers to provide N and enhance the overall nutritional status of low-fertility soils. Nitrate-N fertilizers such as calcium or potassium nitrate, $\text{Ca}(\text{NO}_3)_2$, KNO_3 , are also available, but due to the production costs and lower efficiency of N recovery from NO_3 -based materials, these fertilizer types are primarily used on specialty crops (vegetables, fruits, tobacco) or on crops that are sensitive to NH_3 .

Economics, more than any other factor, often controls the N source selected. In general, fertilizers with higher N contents have lower costs of storage, transportation, handling, and application, and hence are more economic. However, the properties of some high-analysis N fertilizers can increase these costs. For example, anhydrous ammonia, which has the highest N content of any fertilizer material (82% N), requires complex application equipment that must pressurize the gas, convert it to a liquid, and inject the liquefied NH_3 into the soil in a manner that reduces volatilization losses. Ammonia volatilization losses are also a major concern with urea, the highest-analysis solid N fertilizer (45% N), and some type of incorporation is often required to maximize the efficiency of N recovery from this N source. The physical and chemical properties of N sources are not the only factors that influence source selection. In the United States, there are marked

regional preferences for N fertilizers, often related more to the fertilizer manufacturing and transportation infrastructures that have evolved with time rather than to specific requirements of regional cropping systems (Figure 5.27).

Other factors that influence the selection of a N fertilizer include crop management practices (crop type and rotation, tillage, irrigation), soil type and sensitivity to N losses, effect of the N source on soil pH (nitrification is an acidifying process and N fertilizers vary in their potential to decrease soil pH), need to supply other nutrients simultaneously, and the suitability of the material

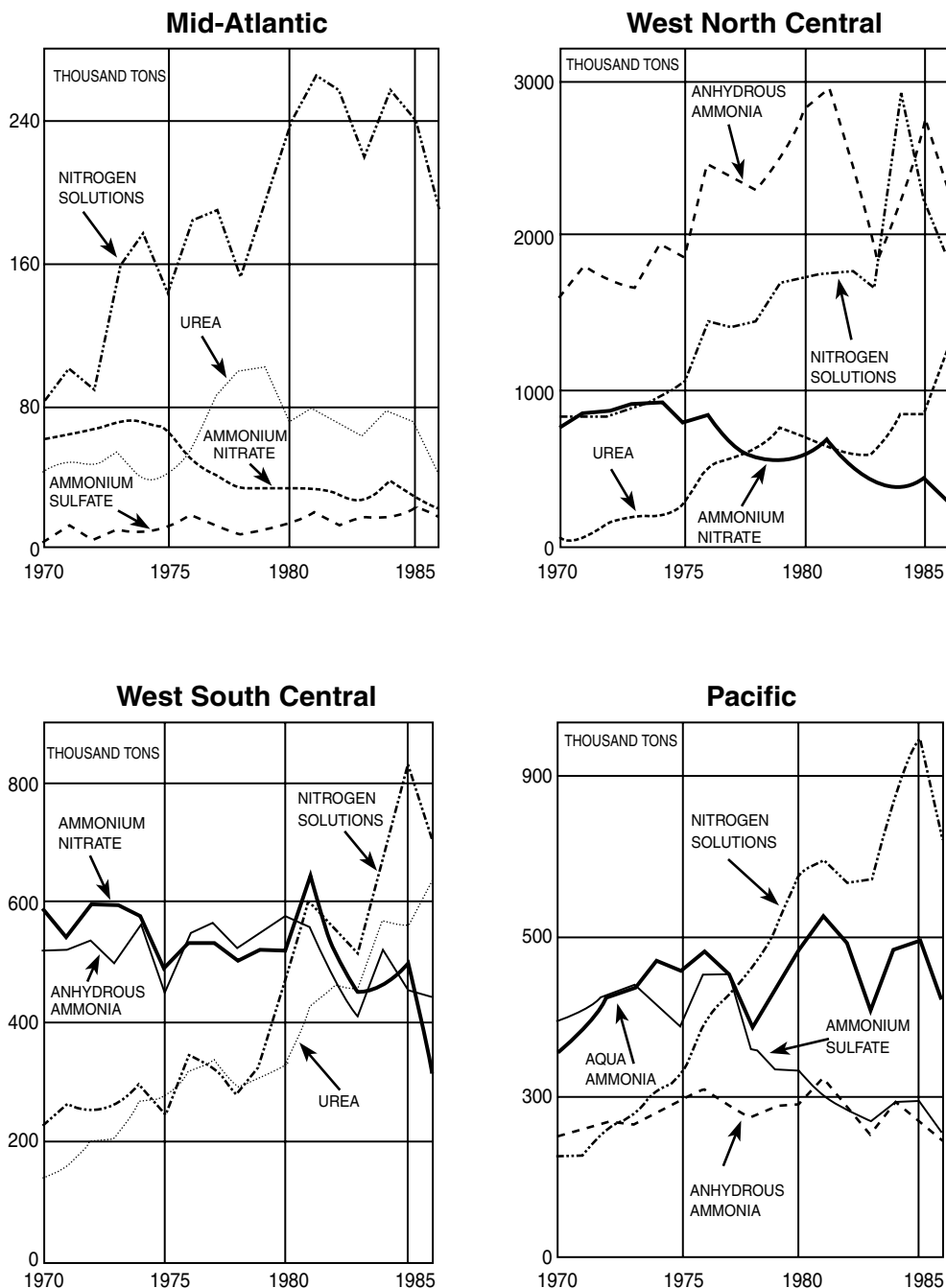


Figure 5.27 Regional preferences and trends in N fertilizer use for 1970–1985. (From Berry and Hargett, 1986.)

for existing application equipment. The implications of these factors for N management are discussed in more detail in Chapter 8.

5.2.5.2 Organic Sources of Nitrogen

A wide variety of organic materials are used as soil amendments, many of which contain appreciable quantities of N. Animal manures, municipal biosolids and wastewaters, composts of municipal solid waste or yard waste, food processing wastes, industrial organics, and crop and forest product residues are the dominant organic by-products produced worldwide. Estimates of the quantity of organic by-products produced annually in the United States exceed 400 million MT/yr. The magnitude of this problem is even more apparent when expressed on a “per-person” basis. For animal manures, municipal solid wastes and biosolids, industrial solid wastes and water treatment sludges, and silviculture residues, the amount generated is roughly equivalent to 900, 550, 450, and 400 kg/person/yr (dry weight basis), respectively. Changes occurring in the United States and other countries are likely to alter the nature and distribution of organic by-products significantly. In many states, landfilling of yard wastes (leaves, grass clippings), which accounted for ~20 to 25% of the landfill volume, is rapidly becoming an unacceptable practice, and is being replaced with the commercial production of yard waste composts. Similarly, a number of municipalities have developed co-composting facilities for biosolids and the organic fraction of municipal refuse. Production of these composts is certain to result in large increases in the amount of organic N applied to soils. Other changes include the production of composted or pelletized animal manures in areas where large excesses of manure, relative to arable land, exist. Movement of animal manures off the farm for use in urban areas or in construction and reclamation projects will likely result in an increased use of these materials in land application programs involving horticultural crops, turf, and revegetation of sites for use by domestic animals and wildlife.

Although all organic by-products contain N, the amount, forms, and availability of N can vary widely. Mean N contents and ranges are available for most organic by-products, but the considerable variability in total and inorganic (e.g., NH_3 , NO_3) N contents of most by-products makes interpretation of analytical results for N or other elements an ongoing problem. Broad generalizations of the N content in organic by-products are probably justified as it has been well documented that certain organic by-products will consistently have higher total N contents than others, as shown in Table 5.7 for animal manures (poultry > swine > dairy > beef) and municipal sludge products (aerobic > anaerobic > composted). The wide range in total N content among similar types of by-products, however, can have significant implications for N loading to soils and crops, as shown in Figure 5.28. In this study, the amount of manure needed to provide a desired amount of N for corn was estimated for poultry manure based on analysis of manure samples from 17 different on-farm storage areas. When the predicted amount of N to be added was compared to the actual N applied, based on analysis of manure samples collected during application, overapplication of 10 to 20 kg N/Mg manure commonly occurred, as did underapplication of 5 to 10 kg N/Mg. Therefore, the accurate application of a recommended manure rate for corn (~5 Mg/ha), based on analysis of the manure, commonly resulted in the application of *excess* manure N approaching the total N requirement of the crop (~100 kg N/ha). Clearly, a more comprehensive approach than simple N analysis and equipment calibration is needed to avoid over- or underapplication of N from organic by-products.

In general, the key to effective use of organic N sources is an understanding of the factors that influence the extent and rate of conversion of organic N to forms that are available for plant uptake or loss to the environment. The availability of N in organic by-products will be influenced by their composition, largely controlled by by-product production and storage practices, and by the chemical and biological changes they undergo following application to the soil. Much of the research in this area has been directed toward identifying the differences in N availability between

Table 5.7 Representative Values for N Content and Availability for Selected Organic By-Products

Organic N Source	Total N (%)	Organic N Mineralized ^a (%)
Animal Manures		
Beef	1.3–1.8	25–35
Dairy	2.5–3.0	25–40
Poultry	4.0–6.0	50–70
Swine	3.5–4.5	30–50
Biosolids		
Aerobic digestion	3.5–5.0	25–40
Anaerobic digestion	1.8–2.5	10–20
Composted	0.5–1.5	(–10)–10
Other By-Products		
Fermentation wastes	3.0–8.0	20–50
Poultry processing wastes	4.0–8.0	40–60
Papermill sludges	0.2–1.0	(–20)–5

Note: Average values from various sources.

^a Organic N mineralized estimated from laboratory incubation studies. Negative values for composts and papermill sludges indicate that immobilization of N occurred.

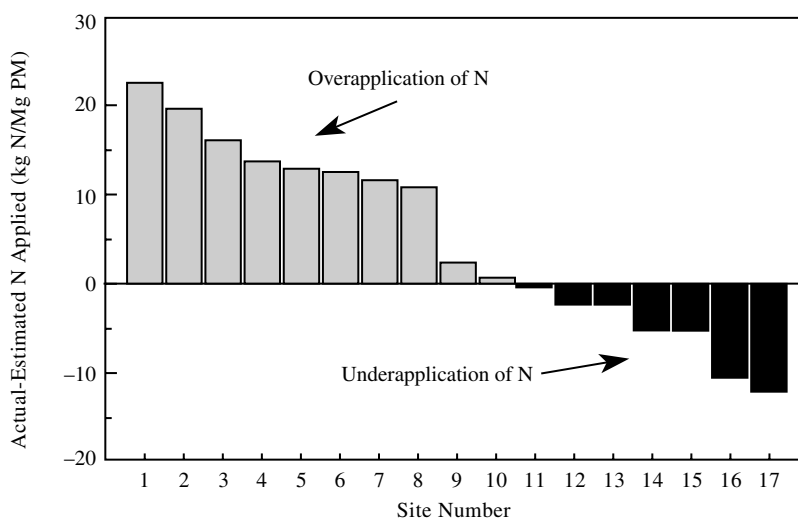


Figure 5.28 The difference between total N based on poultry manure (PM) samples collected during field application and the amount estimated to be applied based on laboratory analyses of stockpiled manure samples. Results of 17 field studies. (From Igo, E. C. et al., *Agron. Abstr.*, p. 155, 1991. With permission.)

various types of by-products and then using by-product properties to predict N availability. As with by-product composition, these studies have shown that by-products can be broadly grouped in terms of organic N availability (Table 5.7). Certain by-products (e.g., poultry manure, aerobically digested biosolids) are not only higher in total N but will provide more N upon

decomposition in the soil than other more stable by-products (e.g., composts, papermill sludges). Simple and complex approaches have been taken to predict N availability. Biosolids have been ranked according to N mineralization potential as waste-activated (40%) > raw and primary (25%) > anaerobically digested (15%) > composted (8%). For some by-products both total and $\text{NH}_4\text{-N}$ must be included to estimate accurately the amount of potentially available N (PAN), as shown in a simple model developed for poultry manures:

$$\text{PAN} = [k_m(\text{N}_o) + e_f(\text{NH}_4\text{-N} + \text{NO}_3\text{-N})] \quad (5.17)$$

where k_m is the percentage of added organic N (N_o) mineralized ($k_m = 40$ to 60%, depending on season of year manure was applied, e.g., winter vs. spring), and e_f is a factor reflecting the efficiency of recovery of $\text{NH}_3\text{-N}$ (20 to 80%, depending on time until incorporation of manure) and $\text{NO}_3\text{-N}$ added in the manure. Some recent research has identified “quick-tests” for PAN in manures. Analysis of broiler litters by near infrared spectroscopy (NIRS) and testing litters for water-soluble organic N (WSN) showed that either of these rapid tests could accurately predict the amount of N mineralized in a sandy loam soil (Figure 5.29). The NIRS method is particularly appealing because this technique is widely used to determine compounds other than N in materials produced by agriculture and the paper, pharmaceutical, and petrochemical industries. Thus, easy access to rapid NIRS testing of manure PAN would be available worldwide.

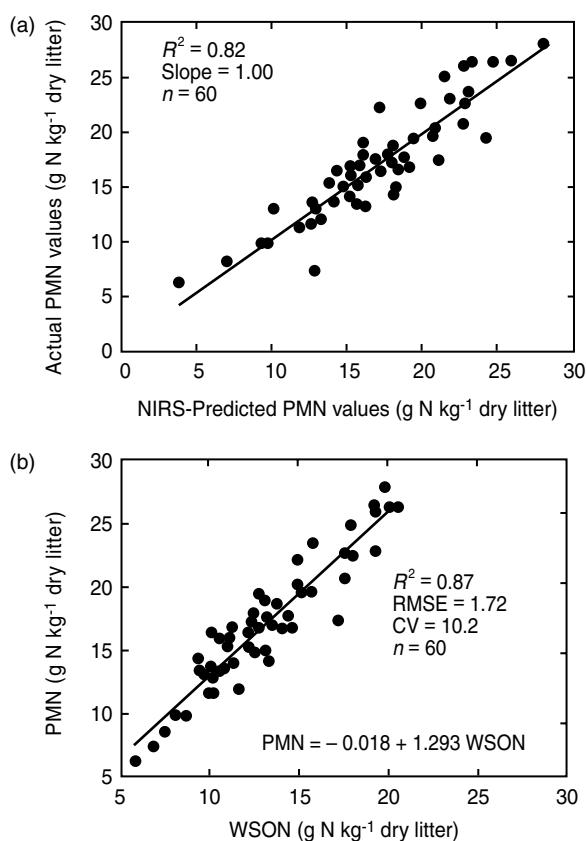


Figure 5.29 Comparison of two means to rapidly measure potentially mineralizable N (PMN) in broiler litters: (a) Near infrared spectroscopy (NIRS) and (b) water-soluble organic N (WSN). (From Qafoku, O. S. et al., *J. Environ. Qual.*, 30, 217–221, 2001. With permission.)

The use of organic by-products as N sources cannot be based on N availability alone. Other nutrients, or nonessential elements, in these materials can determine not only the application rate but also their suitability for various end uses. At present, there are three main aspects of by-product composition that affect short- and long-term use of organic by-products in land application programs: (1) P buildup to excessive levels in by-product-amended soils; (2) the potential for heavy metal contamination of soils, crops, and waters; and (3) the possible adverse environmental impacts of organic pollutants found in organic by-products. Readers are referred to Chapters 6 (Phosphorus), 9 (Trace Elements), 10 (Organic Chemicals), and 13 (Risk Assessment) for more detailed discussions on these topics.

Example Problem 5.4

Fertilizer N recommendations for nonirrigated corn grown in the eastern United States typically range from 100 to 175 kg PAN/ha/year. Based on Equation 5.17, what application rate of poultry manure, in Mg/ha, would be needed to provide 150 kg PAN/ha/year. Assume that the total N content of poultry manure is 4%, the $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations are 0.9 and 0.1%, respectively, and that $k_m = 0.6$ and $e_f = 0.8$.

$$\text{Total N (N}_t\text{) in manure} = \text{N}_o \text{ (organic N)} + \text{N}_i \text{ (inorganic N} = \text{NH}_4\text{-N} + \text{NO}_3\text{-N)}$$

$$\text{Organic N in manure} = (\text{N}_t - \text{N}_i) = [(4\%) - (0.9\% + 0.1\%)] = 3.0\%$$

$$\text{PAN} = [k_m(\text{N}_o) + e_f(\text{NH}_4\text{-N} + \text{NO}_3\text{-N})]$$

$$\text{PAN} = [(0.6 \times 3.0\%) + (0.8 \times 1.0\%)] = 2.6\%$$

$$\text{Manure rate (kg/ha)} = (150 \text{ kg PAN/ha}) \div (0.026) = 5770 \text{ kg manure/ha}$$

$$\text{Manure rate (Mg/ha)} = 5770 \text{ kg/ha} \div 1000 \text{ kg/Mg} = 5.77 \text{ Mg/ha}$$

PROBLEMS

- 5.1 List all the impacts that N used in agriculture can have on other sectors of the environment. Describe the pathways by which N in agricultural soils can move from the soil to air and water.
- 5.2 Some areas in the United States have reported very high $\text{NO}_3\text{-N}$ concentrations in groundwaters that are used for irrigation. If irrigation water that has a $\text{NO}_3\text{-N}$ concentration of 28 mg $\text{NO}_3\text{-N/L}$ and 2 cm of irrigation water/ha is applied to a corn crop ten times during the growing season, what is the total amount of soluble $\text{NO}_3\text{-N}$ added to the crop via irrigation, in kg/ha?
- 5.3 The EPA has established “ecoregional nutrient criteria” for surface waters. Locate the Web site for these nutrient criteria (<http://www.epa.gov/waterscience/criteria/nutrient/database/>) and query the database for your state. What type of water quality data are available? Access the database and compare the $\text{NO}_3\text{-N}$ concentrations in various water body types between counties in your state. Next, compare differences between states with widely differing land uses (e.g., row crop agriculture in Iowa vs. rangeland in Wyoming). What explanations exist for the differences in water quality?
- 5.4 Hypoxia in the Gulf of Mexico is an international environmental issue, with water quality problems related to land use in much of the United States. Visit the EPA Web site that outlines the current action plans for hypoxia (<http://www.epa.gov/msbasin/actionplan.htm#Framework>). Explain the meaning of the term “adaptive management” and why it is the approach chosen by those attempting to reduce hypoxia in the Gulf.
- 5.5 The long-term use of animal manures can increase the N-supplying capacity of soils and decrease the need for inputs of fertilizer N. A recent study (Gordillo and Cabrera, 1997) evaluated the mineralization of N in ten soils amended with poultry litters, using Equation 5.7. The authors reported the following mean values: $\text{N}_f = 11.0 \text{ g N/kg}$, $\text{N}_s = 13.8 \text{ g N/kg}$, $k_f = 2.6/\text{day}$, and $k_s = 0.04/\text{day}$. Using

- Equation 5.7 and these values, calculate the amount of N that would be mineralized from a soil amended with poultry litter after 1, 7, 14, 21, 42, and 84 days. What are the implications of this mineralization pattern for poultry litter management?
- 5.6 If the Q_{10} value for the rate of N mineralization in the study in Problem 5.5 was 2.0, how much more N would be mineralized in a poultry litter amended soil in 7 days if the soil temperature was increased from 15°C (a cool spring application) to 35°C (a hot summer application)? (See Section 5.2.1 for definition and discussion of Q_{10} values).
 - 5.7 It has been estimated that 30% of the N entering a poultry farm in feed is lost to the atmosphere in NH_3 emissions from the poultry houses during the growth of the chickens. It requires about 5 kg of feed that has an average N content of 2.8% to produce one broiler chicken. Assume that a poultry farm has two poultry houses, each with a capacity of 20,000 chickens per flock, and produces six flocks of chickens per year. How many kg of N are lost from this farm as NH_3 each year? If 75% of the NH_3 that was emitted from the total production facility was deposited on the 10 ha of cropland closest to the farm, how much lime (in Mg/ha) would be needed to neutralize the acidity that resulted from the nitrification of this NH_3 (assume that it takes 0.9 kg of agricultural-grade limestone to neutralize the acidity produced by 0.45 kg of NH_3).
 - 5.8 Many corn farmers in the eastern United States now use minimum or no-tillage farming practices to reduce soil erosion, conserve soil moisture (crop residue acts a mulch to reduce evaporative losses of soil water), and build soil organic matter. To save time, these farmers may also spray a mixture of urea-ammonium NO_3 fertilizer and preemergence herbicides onto the surface of the soil immediately after planting. Explain (a) how and why this practice would affect the potential for N losses by ammonia volatilization; (b) what the implications are for corn production; and (c) how timing the application relative to expected rainfall could affect ammonia loss and corn yields (see Table 5.3).
 - 5.9 Review Figure 5.16 and explain why corn grown in a field where the pharmaceutical by-product was injected in this manner might exhibit N deficiency. How could you prevent N deficiency by changing the application method for the by-product?
 - 5.10 It has been claimed that organic farming practices will reduce leaching losses of NO_3^- . A review of the scientific literature by Kirchmann and Bergstrom (2001; see Supplementary Materials) disputes this and states that there is no evidence that organic farming will reduce NO_3^- leaching; in fact, in some cases, increased leaching losses occurred. Explain, based on the principles of the soil N cycle, why organic farming could reduce, or increase, NO_3^- leaching to groundwaters.
 - 5.11 The fertilizer N recommendation for a wheat crop is 100 kg N/ha. How much of each of the following fertilizer materials would you need to apply, in kg/ha, to provide this amount of available N to the wheat: ammonium nitrate, ammonium sulfate, urea, and UAN solution. (Assume the density of a 30% UAN solution is 1.3 kg/L.)
 - 5.12 Assume you are working as a consultant for an organic farming operation that produces vegetables and wheat for bread making. The farm has access to a ready supply of poultry manure from a nearby farm and composted biosolids from a small municipality. The operation asks you what application rate, in Mg/ha, of each material would be needed to provide 150 kg N/ha for their vegetable crops and 90 kg N/ha for their wheat. Using Equation 5.17 and the following information, determine the application rates required for: (a) poultry manure (total N = 5.0%, $\text{NH}_4\text{-N}$ = 1.0%, k_m = 0.80, e_f = 0.80 if incorporated within 1 day, 0.40 if incorporated within 1 week); (b) composted biosolids (total N = 2.0%, $\text{NH}_4\text{-N}$ = 0.05%, k_m = 0.15, e_f = 0.90 if incorporated within 1 day, 0.60 if incorporated within 1 week). The workers also ask you to give them a general overview of any other factors to consider when deciding between the two organic sources of N. What is your response?

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Soil Phosphorus and Environmental Quality

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6.1 PHOSPHORUS AND THE ENVIRONMENT

Phosphorus (P) is essential to all forms of life on earth and has no known direct toxic effects to humans or animals. Most of the Earth's P is conserved in terrestrial soils and in the sediments in freshwaters, estuaries, and oceans. From an agricultural perspective, maintaining soil P concentrations in an optimum range for plant growth is necessary to sustain soil fertility and ensure the production of food crops and a wide array of other types of plants (e.g., fiber and oil crops, medicinal and horticultural plants). Environmental concerns associated with P center on its stimulation of biological productivity in aquatic ecosystems. In most freshwater systems, primary productivity (e.g., the growth of algae or aquatic plants) is limited by inadequate levels of P. External inputs of P from urban wastewater systems, surface runoff, or subsurface groundwater flow can remove this limitation and stimulate the growth of aquatic organisms to ecologically undesirable levels. Total P concentrations of >100 µg P/L (ppb) are regarded as unacceptably high in most surface waters, and concentrations as low as 10 µg P/L can cause environmental problems in some waters, primarily through eutrophication.

Eutrophication is defined as “an increase in the fertility status of natural waters that causes accelerated growth of algae or water plants.” Figure 6.1 is a photograph of a eutrophic canal next to a pasture in the Netherlands. Eutrophication is not caused by inputs of P alone, but by a complex interaction among nitrogen (N), P, environmental conditions (temperature, salinity, light), and the physical and hydrologic characteristics of different types of surface waters (streams vs. lakes vs. estuaries). For example, N limits primary productivity more in estuaries and other coastal waters than P, particularly in summer months. It is also recognized that the nutrient concentrations in a water body that will lead to eutrophication vary geographically, due to differences in geology, physiography, vegetation, climate, soils, wildlife, and hydrology. Recently, the U.S. Environmental Protection Agency (EPA) defined 14 *nutrient ecoregions* in the United States based on these characteristics and proposed quantitative nutrient criteria for causative (N and P concentrations) and response (chlorophyll *a* and turbidity) variables important to assessing, monitoring, and preventing eutrophication (see <http://www.epa.gov/waterscience/criteria/nutrient/ecoregions/> for more details) (Figure 6.2a). The nutrient criteria values represent conditions in surface waters that have experienced minimal impact by human activities and are thus suggested as baseline numbers that can guide watershed-scale efforts to protect and restore water quality. In a related effort, the U.S. Geological Survey (USGS) recently summarized, through its National Water Quality Assessment Program (NAWQA), the relationship between total P inputs and total P concentrations in streams for agricultural, urban, and mixed and land uses (Figure 6.2b).

The negative effects associated with eutrophication of surface waters are important from ecological, economic, and animal and human health perspectives. As nutrient inputs to surface waters gradually increase, the trophic state of the water body passes through four stages of eutrophication: *oligotrophic*, *mesotrophic*, *eutrophic*, and *hypereutrophic* (Figure 6.3a). At each stage, progressive changes in the ecology of the water body occur that degrade habitat quality, reduce biodiversity, decrease economic value, and impair recreational uses (Figure 6.3b; also see Section 6.1.1).

If we are to manage soil P to prevent eutrophication and sustain agricultural productivity, we must address the following questions:

- What are the characteristics of a water body that control eutrophication? Is eutrophication limited mostly by P, or by N, or by both nutrients?
- What are the natural inputs of P into a water body, from groundwater discharge, erosion and runoff from natural areas, and atmospheric deposition?



Figure 6.1 (Color figure follows p. 242.) Eutrophic canal next to a pasture in the Netherlands.

- Do anthropogenic P inputs to a water body come from point- or nonpoint-source pollution? When and where do inputs of P from agricultural and urban sources affect water quality?
- How does the soil P cycle affect the availability of P for transport to water bodies? When does soluble P become important, as well as particulate P?
- What are the dominant transport mechanisms operational between the sources of P and the water body (e.g., erosion, surface/subsurface runoff, channel processes) and how do they vary with land use, management, and seasonal climatic patterns?
- What management practices can be used to reduce P loading to a water body from all sources, urban and rural, point and nonpoint? How can we develop an integrated, economically feasible approach to reduce P loading to water bodies?

6.1.1 Eutrophication: The Role of Phosphorus

As the sole environmental impact of P is its role in eutrophication, a clear understanding of this process is essential to the development of sound strategies for P management. Eutrophication has long been known to affect freshwaters, such as lakes and rivers, and recently has become an international ecological problem for coastal waters (estuaries and coastal ocean regions).

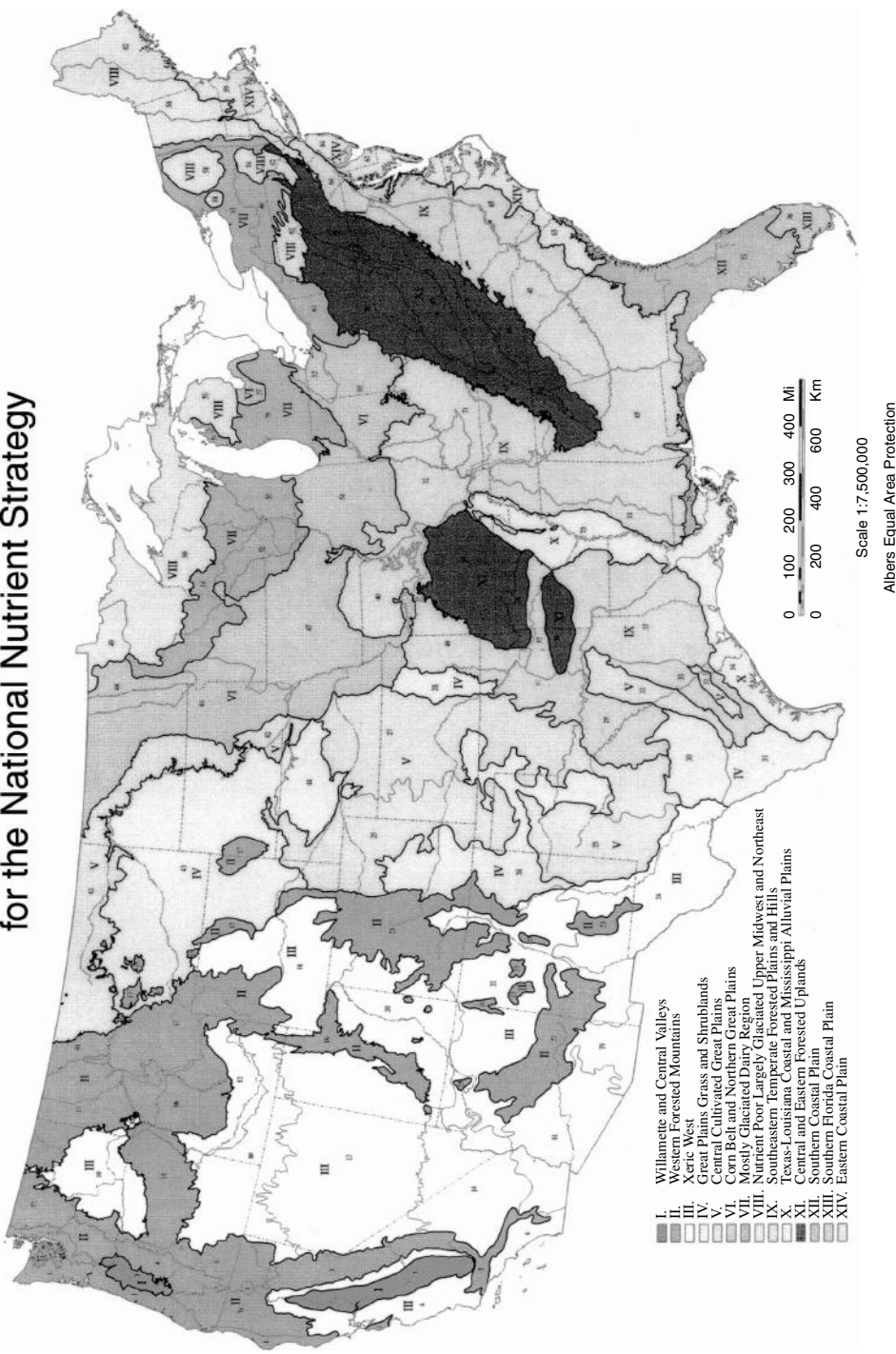
In oligotrophic lakes, soluble and sediment-bound nutrient (N, P) concentrations are low and limit the growth of algae and other water plants. These lakes are normally deeper and have adequate oxygen (O_2) levels even in the summer when photosynthesis and temperatures favor maximum plant growth. They also have a high degree of species diversity for plants and animals. However, oligotrophic lakes, because of their low nutrient concentrations, also have low biological productivity and, if used for economic production of fish, may even require some fertilization to sustain a fishing industry. Alterations in the ecosystem (construction of wastewater treatment plants, conversion of land from forested to agricultural or urban use) can increase inputs of nutrients to oligotrophic lakes, stimulating the growth of algae and other water plants, initiating and accelerating the eutrophication process (Figure 6.3). For example, as shown in Figure 6.4 converting land that is 90% forested to 90% agricultural could result in a threefold increase in total P loss in runoff.

Similar causes and problems associated with eutrophication are increasingly being reported in coastal waters. The phenomenon in these ecosystems is commonly referred to as *hypoxia*, defined as a situation where the supply (or consumption) of O_2 declines below the concentration that can sustain the life of aquatic fishes and invertebrates. While the actual O_2 concentration varies between waters and organisms, if dissolved O_2 is <2 mg/L, most conditions associated with hypoxia are commonly observed. For reference, the O_2 concentration in oxygenated waters is 10 to 12 mg/L. As in freshwaters, nutrients fuel primary production (new organic matter) that, because of the relatively shallow nature of most coastal waters, settles quickly to the bottom. Initially, the nutrients in this organic matter may stimulate fisheries production, but with time, hypoxic conditions can cause a decline in fish harvest, as seen in Figure 6.5 for some important coastal waters. In the United States, a 20,000-km² hypoxic zone has been reported in the northern Gulf of Mexico and linked to increases in nutrient delivery from the Mississippi and Atchafalaya Rivers since the late 1950s. Nitrogen loading from the Mississippi River alone was reported to have more than doubled from the 1950s to 1980s (Rabalais et al., 2001).

Eutrophic waters are widely regarded as undesirable, for many reasons (see Tables 2.6 and 2.7). Once eutrophic conditions are established, algal blooms and other ecologically damaging effects can occur, including low dissolved O_2 levels, excessive aquatic weed growth, increased sedimentation, and greater turbidity. Decreased oxygenation is the primary negative effect of eutrophication because low dissolved O_2 levels seriously limit the growth and diversity of aquatic biota and, under extreme conditions, cause fish kills. The increased biomass resulting from eutrophication causes the depletion of O_2 , especially during the microbial decomposition of plant and algal residues. Under the more turbid conditions common to eutrophic lakes, light penetration into lower depths of the water body is decreased, resulting in reduced growth of submerged

(a)

Draft Aggregations of Level III Ecoregions
for the National Nutrient Strategy



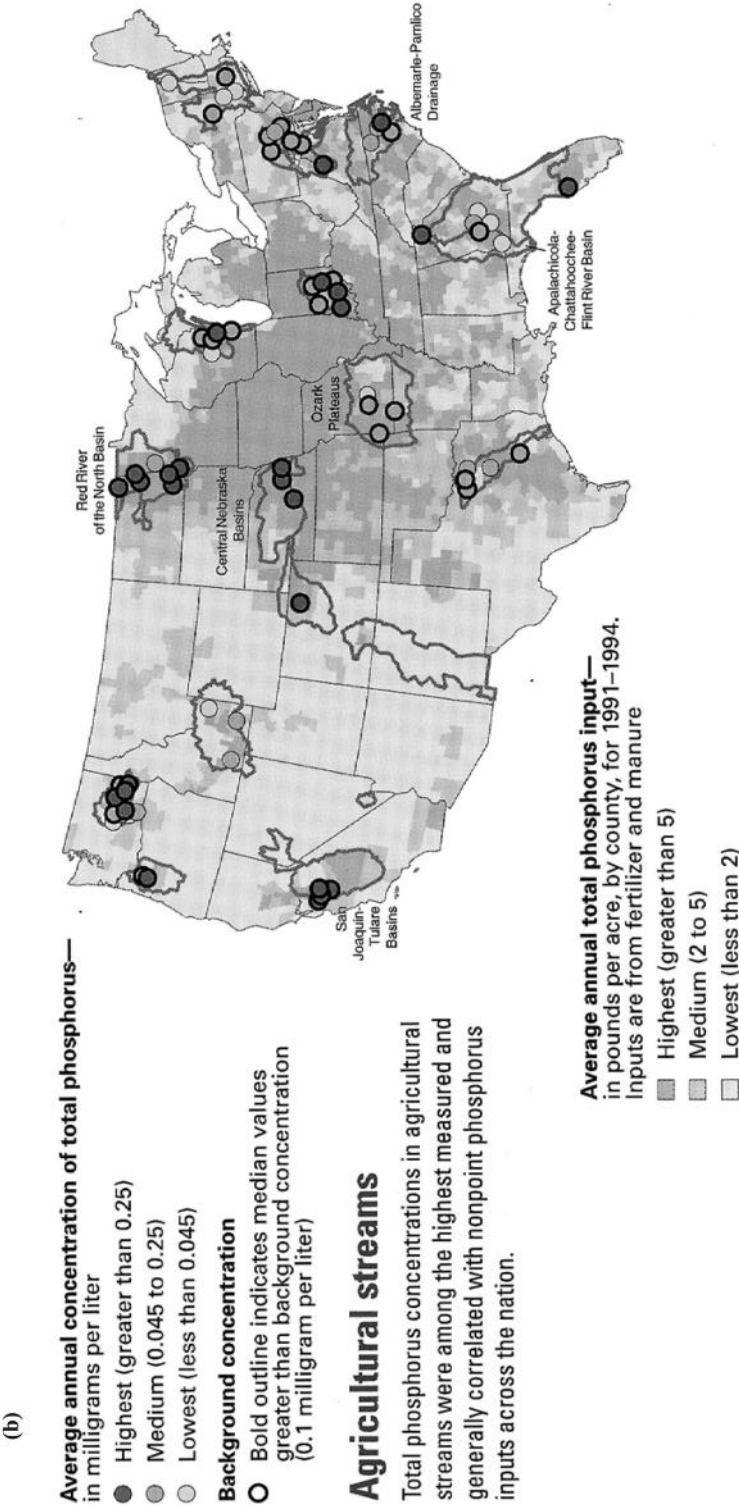


Figure 6.2 (a) Nutrient ecoregions established for the United States by the EPA (www.epa.gov/waterscience/standards/ecomap.html); (b) a national ranking of total P concentrations in streams from agricultural areas compared to total P inputs in fertilizer and manure. (From USGS, 1999.)

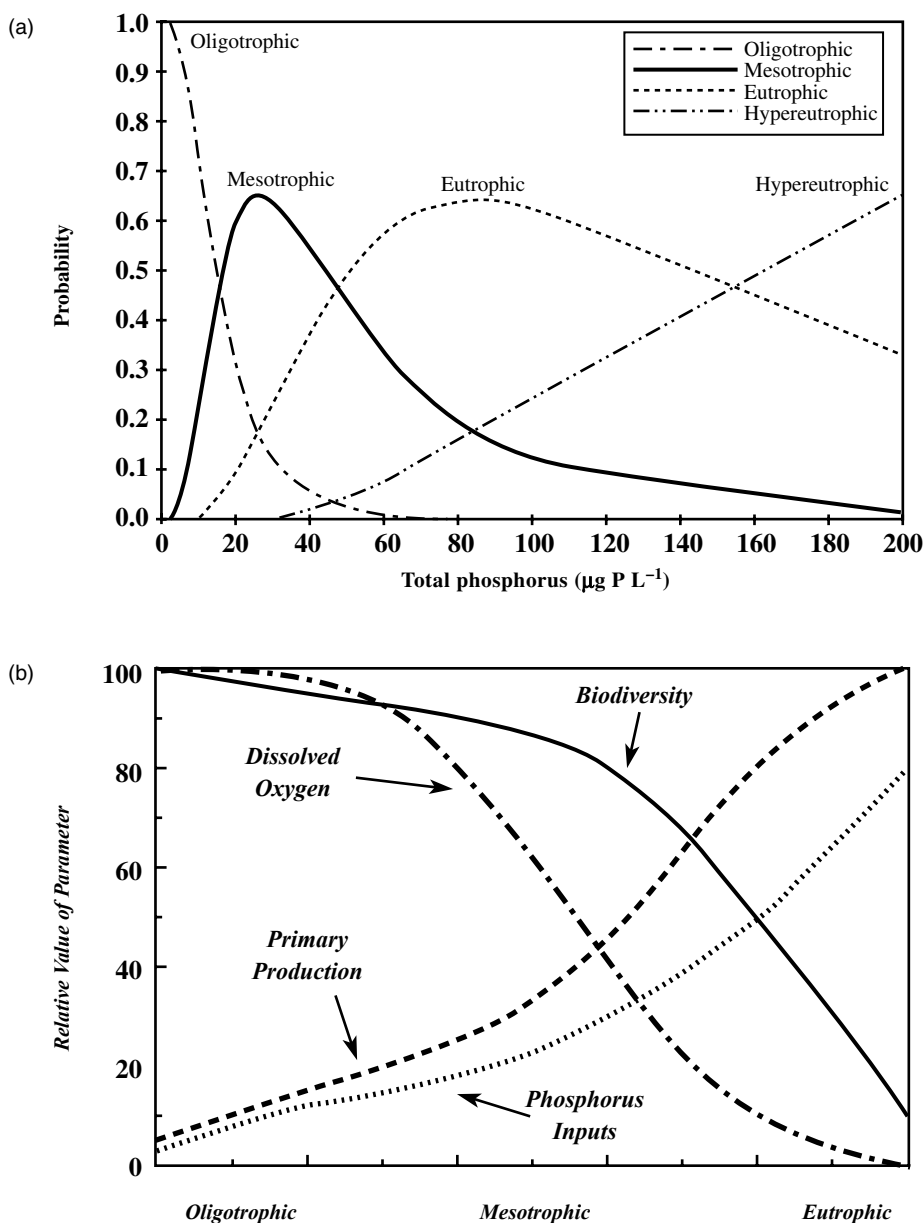


Figure 6.3 (a) Probability distribution for lake trophic status compared to annual mean total phosphorus concentration. (From Foy, R. H. and P. J. A. Withers, *The Contribution of Agricultural Phosphorus to Eutrophication*, Proc. 366, Fertilizer Society, Petersborough, U.K., 1995. With permission.) (b) Overview of the changes that occur when freshwaters become eutrophic. (Adapted from Correll, 1998.)

aquatic vegetation (SAV) and benthic (bottom-living) organisms. The SAV are essential components of a healthy aquatic ecosystem because they filter pollutants; provide food for waterfowl and habitat for shellfish; reduce wave energies and help settle sediments, which reduces turbidity in the water column; and absorb nutrients that promote algal blooms. Restoring SAV is a vital step in improving water quality, as evidenced by the efforts of the Chesapeake Bay Program to protect existing beds and plant new ones, with a goal of 75,000 ha in the bay by 2010, compared to 15,000 in 1984. In addition to ecological damage, eutrophication can

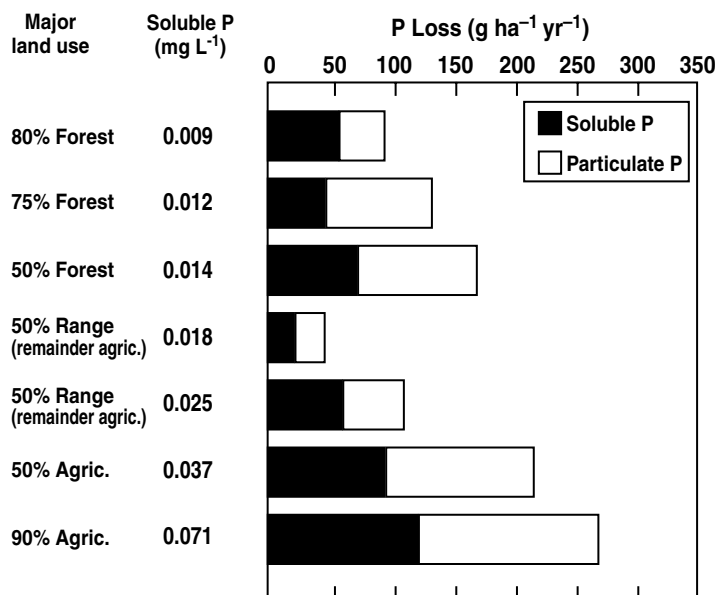


Figure 6.4 Effect of land use on the loss of soluble and particulate P from soils. (From Sharpley, A. N. and A. D. Halvorson, in *Soil Processes and Water Quality*, R. Lal, Ed., Advances in Soil Science, Lewis Publishers, Boca Raton, FL, 1994.)

increase the costs of maintaining surface waters for recreational and navigational purposes. Surface scums of algae, foul odors, insect problems, impeded water flow and boating due to aquatic weeds, shallower lakes that must be dredged to remove sediment, and disappearance of desirable fish communities are among the most commonly reported undesirable effects of eutrophication.

In some cases eutrophication also causes ecological changes that may affect animal and human health. Recent concerns about the effects of harmful algal blooms (HABs or “red tides”) on human and ecosystem health have heightened public awareness of the problems of eutrophication and of the needs to reduce nonpoint-source pollution of surface waters by N and P. Documented impacts of HABs include mass mortalities of farmed fish and shellfish, human illness and death from toxic seafood or from toxin exposure through inhalation or water contact, illness and death of marine mammals, seabirds, and other animals, and alteration of marine habitats (Anderson et al., 2002). Some species of HAB can produce neurotoxins and hepatotoxins that have been reported to cause deaths of livestock and wildlife and, although rare, humans (Chorus and Bartram, 1999). It has also been reported that algal blooms contributed to the formation of dangerous trihalomethanes during the chlorination process in water treatment plants.

The environmental impacts of eutrophication on water quality, and now perhaps on human and animal health, have resulted in major efforts to develop management strategies to reduce nutrient inputs to surface waters and, where possible, to reclaim eutrophic water bodies. It is important to remember that controlling eutrophication requires that both N and P enrichment of surface waters be minimized, although in most freshwaters biological productivity is limited by P, not N. Studies have shown that the ratio of N:P in the water body (referred to as the “Redfield ratio”) is an important indicator of which nutrient is limiting eutrophication. If the Redfield ratio is >16:1, P is most likely the limiting factor for algal growth; lower ratios indicate that N is of greater importance. The eutrophication threshold for most P-limited aquatic systems (~20 to 100 µg P/L) is much lower than for N (500 to 1000 µg N/L). Water bodies with naturally low P concentrations will, therefore, be highly sensitive to external inputs of P from agricultural runoff, domestic wastewater treatment systems, urban storm water discharge, and industrial wastewaters. Some countries have begun to

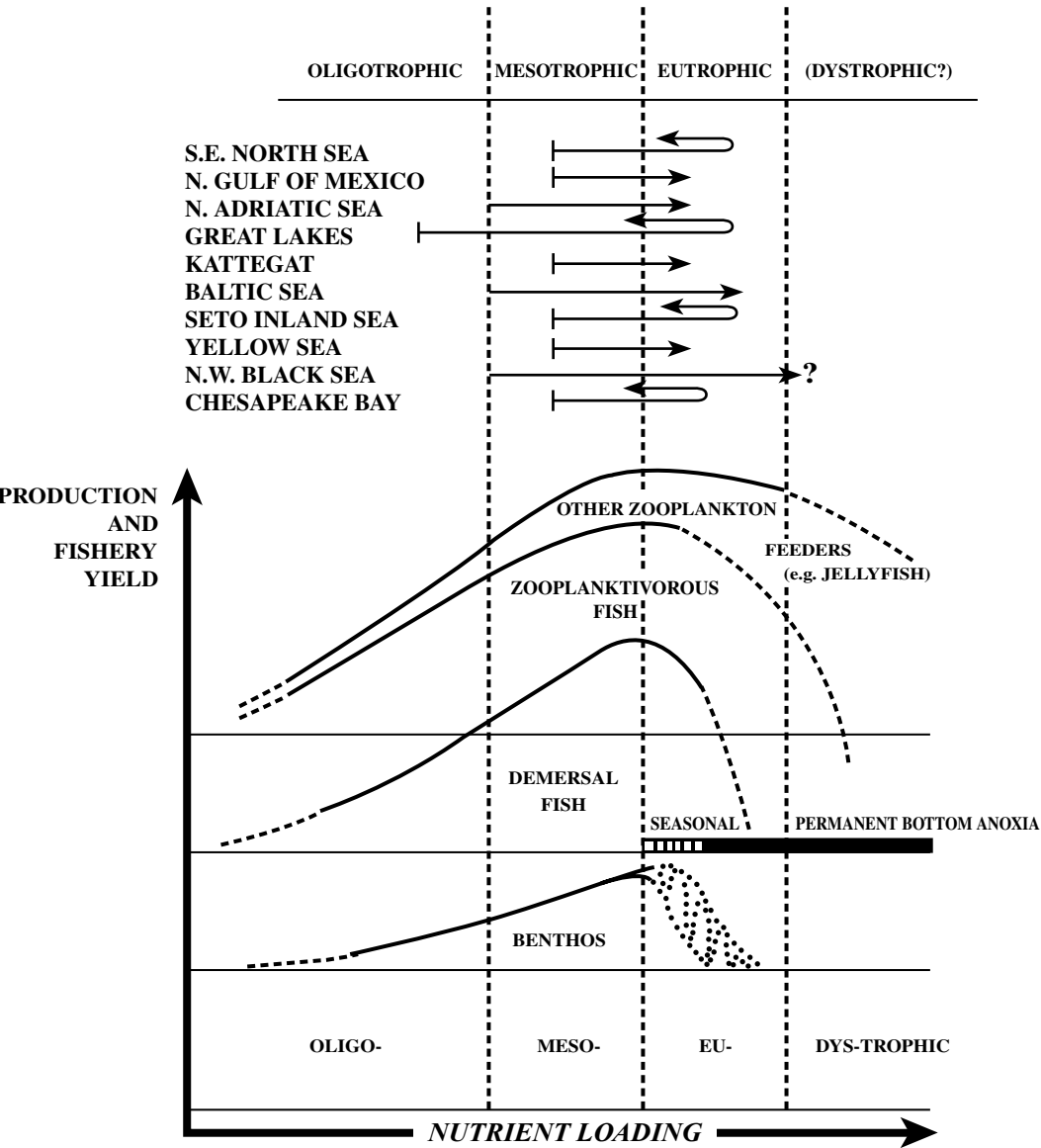


Figure 6.5 Evaluation of fishery responses to increased nutrient loading for a number of important coastal waters in the world. (Note: Dystrophic waters are defined as those with no or extremely low levels of productivity). Each curve represents a general guild of species and their reaction to increasing nutrient supplies. The top part of the figure lists recent trends for various systems around the world. Vertical dashed lines separate general categories of organic production that result from different levels of nutrients. (From Diaz, R. J., *J. Environ. Qual.*, 30, 275–281, 2001. With permission.)

establish P concentrations above which surface waters are considered sufficiently eutrophic to mandate efforts to reduce point- and nonpoint-P loading, similar to the nutrient ecoregion criteria shown in Table 6.1. For example, the European Community Urban Wastewater Treatment Directive defined eutrophic waters as those with a molybdate reactive P (MRP) concentration >100 µg P/L and recent Irish legislation set an even more restrictive P concentration of 30 µg MRP/L (Withers et al., 2000). Restoration efforts for the Everglades National Park in Florida use 10 µg total P/L as the limiting value for protection and restoration of natural flora and fauna in this nutrient-impacted ecosystem. Achieving these very low P concentrations in streams and rivers draining

Table 6.1 Nutrient Criteria Established by the EPA for the 14 Ecoregions in the United States (see Figure 6.2)

Parameter	Nutrient Ecoregion													
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Lakes and Reservoirs														
Total P (µg/L)	na	8.8	17.0	20.0	33.0	37.5	14.8	8.0	20.0	na	8.0	10.0	17.5	8.0
Total N (mg/L)	na	0.10	0.40	0.04	0.56	0.78	0.66	0.24	0.37	na	0.46	0.52	1.27	0.32
Chlorophyll a (µg/L)	na	1.9	3.4	2.0	2.3	8.6	2.6	2.4	4.9	na	2.8	2.6	12.4	2.9
Secchi (m)	na	4.5	2.7	2.0	1.3	1.4	3.3	4.9	1.5	na	2.9	2.1	0.8	4.5
Rivers and Streams														
Total P (µg/L)	47.0	10.0	21.9	23.0	67.0	76.3	33.0	10.0	36.6	128 ^a	10.0	40.0	na	31.3
Total N (mg/L)	0.31	0.12	0.38	0.56	0.88	2.18	0.54	0.38	0.69	0.76	0.31	0.90	na	0.71
Chlorophyll a (µg/L)	1.8	1.1	1.8	2.4	3.0	2.7	1.5	0.6	0.9	2.1	1.6	0.4	na	3.8
Turbidity (FTU/NTU)	4.3 ^F	1.3 ^N	2.3 ^F	4.2 ^F	7.8 ^F	6.4 ^F	1.7 ^N	1.3 ^F	5.7 ^F	17.5 ^F	2.3 ^N	1.9 ^N	na	3.0 ^F

Note: F = turbidity expressed in FTU units; N = turbidity expressed in NTU units.
^aUnusually high value that may be a statistical anomaly or may reflect a unique condition; further regional investigation needed.

agricultural and urban lands will require extensive improvements in water treatment infrastructure used by point sources (e.g., wastewater treatment plants) and widespread implementation of best management practices (BMPs) to reduce nonpoint-P losses.

Example Problem 6.1

A small coastal estuary near a community has begun to show signs of eutrophication. Water quality measurements show the total P concentration in the estuary is 3.6 $\mu\text{mol/L}$ and the total N concentration is 0.88 mg/L. Based on the Redfield ratio, which nutrient limits primary productivity in this estuary?

$$\text{Redfield ratio} = \frac{\text{Total N } (\mu\text{g/L})}{\text{Total P } (\mu\text{g/L})}$$

$$\text{Total N} = \frac{0.88 \text{ mg N}}{\text{L}} \times \frac{1000 \mu\text{g}}{\text{mg}} = \frac{880 \mu\text{g N}}{\text{L}}$$

$$\text{Total P} = \frac{3.6 \mu\text{mol P}}{\text{L}} \times \frac{30.97 \mu\text{g P}}{\mu\text{mol}} = \frac{111 \mu\text{g P}}{\text{L}}$$

$$\text{Redfield ratio} = \frac{880 \mu\text{g N/L}}{111 \mu\text{g P/L}} = 7.9$$

Nitrogen is the limiting nutrient since the Redfield ratio is less than 16.

Strategies to reduce P loading must consider the nature of the P source as well as the sensitivity of the water body to eutrophication. Even natural ecosystems, such as forests or grasslands, normally considered to be low in P fertility, may provide enough P from overland and subsurface flow to alter the nutrient balance of a water body that is on the threshold of eutrophication. Controlling P inputs from natural areas is generally not feasible, with the possible exception of commercial forestry operations where erosion control practices can reduce sediment loads to surface waters. In contrast, P discharge from a point source (e.g., wastewater treatment plant) may be easy to identify and control, but costly to correct due to the expenses associated with technological improvements to municipal or industrial wastewater treatment plants. Conversely, reducing P loading to surface waters from nonpoint sources, such as runoff from an urban or agricultural watershed, is often limited not by technological costs, but by the difficulties associated with implementing improved nutrient management practices over a large area with diverse agricultural (or rural and industrial) enterprises.

The relative magnitudes of these P inputs and the complexities involved in reducing P loading to water bodies are shown in Figure 6.6, which provides a broad view of the impact of civilization on a watershed-scale P “budget” (P inputs – P outputs). For the Lake Ringsjon watershed, a large P surplus exists, with P inputs from all sources (municipal and rural sewage, manures, fertilizers, runoff from urban and forested areas) totaling ~512,000 kg/year and P outputs (crops, groundwater) ~150,000 kg/year. Although all P inputs do not directly enter the lake, as much of the P is stored in soils in sparingly soluble forms, it seems clear that long-term nutrient enrichment of this lake is due to the excess of P coming from agricultural and urban activities in the watershed. Another example of the effects of land use on watershed-scale point- and nonpoint-source P loading is given in Table 6.2 for Delaware’s Inland Bays, a coastal watershed dominated by a nutrient-intensive poultry–grain agriculture and a large tourism industry.

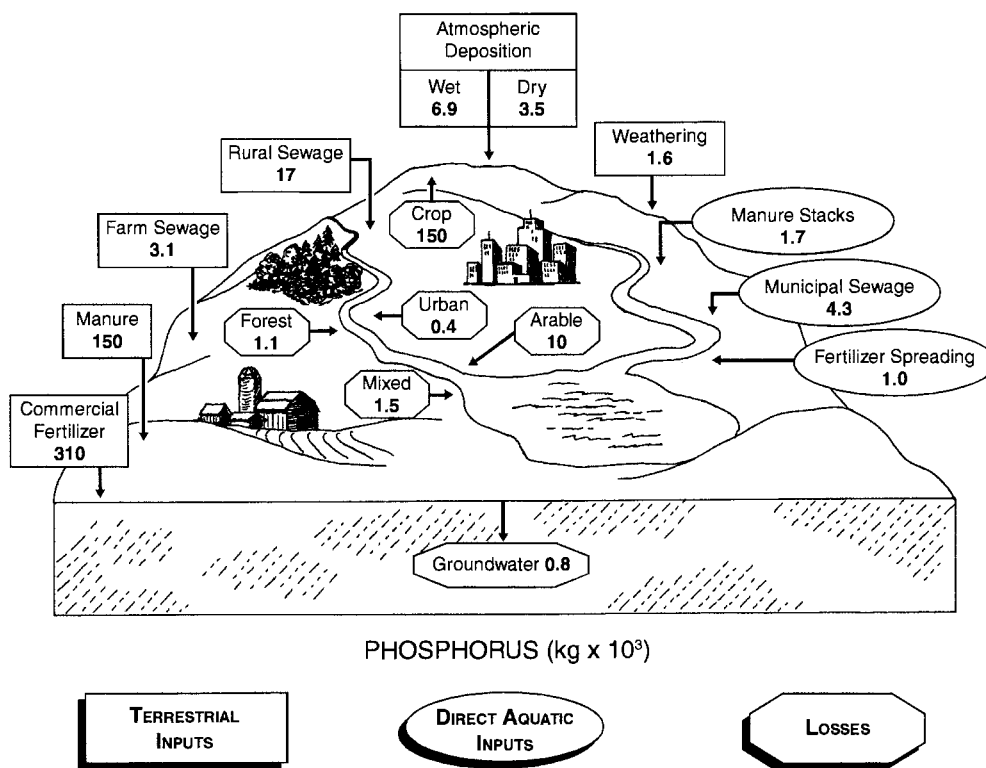


Figure 6.6 Phosphorus budget for agricultural and urban areas of the Lake Ringsjön (Sweden) watershed. (Adapted from Ryding et al., 1990.)

Agriculture is clearly the largest single source of P to the Inland Bays (~37% for the entire watershed), perhaps expected because it is the single largest land use (~45%). However, the large inputs of P from nonagricultural activities (34% from urban runoff, boating, septic tanks, and point sources combined) and natural inputs (29% from forests, wetlands, and rainfall) point to the need to develop comprehensive management practices that reduce P export from all land uses if we are to protect and improve water quality.

6.1.2 Environmental Impacts of Soil Phosphorus

While many point and nonpoint sources of P have the potential to induce eutrophication in surface waters, the focus of this chapter is on soil P and the processes that control its solubility, bioavailability, and potential transfer from land to water. The management practices used to sustain agricultural productivity and minimize P loss are described in detail in Chapter 8.

The total quantity of P in a lake or other surface water body will be controlled by the balance between the inputs from external sources (agriculture, urban runoff, point sources) and the outputs as water drains from the lake via rivers, streams, or other watercourses. A net increase in P will increase the likelihood of eutrophication, but the cycling of P between soluble, organic, and sediment-bound forms within any aqueous ecosystem will regulate the bioavailability of P and thus the extent of eutrophication that occurs. Therefore, insofar as soil P is concerned, its importance in eutrophication will be regulated by the chemical, biological, and physical reactions that control P solubility in soils, the transport processes that move soluble and particulate P (organic and inorganic) to surface waters, and the effects of the chemistry and biology of the water body on P availability to aquatic biota. An overview of these complex phenomena is given in Figure 6.7,

Table 6.2 Influence of Land Use on Phosphorus Loading to the Three Subwatersheds of Delaware's Inland Bays

Source of Phosphorus	Phosphorus Load to Inland Bays' Subwatershed (kg/year) (% total P load in subwatershed)		
	Rehoboth	Indian River	Little Assawoman
Point Sources	5,300 (25)	5,820 (16)	No point sources
Nonpoint Sources			
Groundwater discharge			
Urban	1,700 (8)	2,560 (7)	560 (7)
Agricultural	4,910 (24)	11,030 (30)	2,700 (34)
Forest	2,700 (13)	5,700 (16)	1,000 (13)
Erosion and runoff			
Urban	420 (2)	640 (2)	300 (4)
Agricultural	1,220 (6)	2,760 (8)	1,440 (18)
Forest	680 (3)	1,420 (4)	540 (7)
Other			
Rainfall	2,500 (12)	3,300 (9)	910 (12)
Boating	35 (<1)	47 (<1)	5 (<1)
Septic tanks	1,370 (7)	3,310 (9)	440 (6)
Total	20,835	36,587	7,895
Land Use (%)			
Subwatershed (ha)	Urban	Agriculture	Forest and Wetlands
Rehoboth (16,500)	15	41	44
Indian River (39,000)	9	44	47
Little Assawoman (8,500)	11	54	35

Source: Adapted from Ritter, 1992.

which summarizes the movement of P in soils, the main transport pathways for P from land to water, and the major transformations of P in aquatic ecosystems.

In brief, water moving across or through soils dissolves or physically detaches inorganic or organic forms of P, initiating the transport process. The dissolved or particulate P can then either enter a flowing water body (stream, river) where it can be deposited as sediment or be carried into standing waters (lakes, ponds, reservoirs), and, eventually, to coastal ecosystems and oceans. Phosphorus can also leach downward in the soil, perhaps to a tile drainage system or to shallow groundwaters, where subsurface transport can then discharge the P into surface waters. Once in a lake, soluble P is immediately available for uptake by aquatic organisms such as algae, while much of the particulate P is removed from the lake by deposition as sediment. It is important to note that P bound to sediments in streams, lakes, or coastal waters may later become available for biological uptake. This can occur when P uptake by aquatic plants depletes soluble P, when sediments are reduced under anoxic conditions, or when climatic conditions cause lake turbulence and resuspension of sediments. The complex interaction of sediments and the overlying water column is shown in Figure 6.8, which describes the role of nutrient loading and bottom sediments on the “degradation and restoration trajectories” for the Chesapeake Bay. Clearly, an in-depth understanding of the chemistry, biology, and physics of P in soil and aquatic environments is needed to design management practices that will reduce P impacts on water quality.

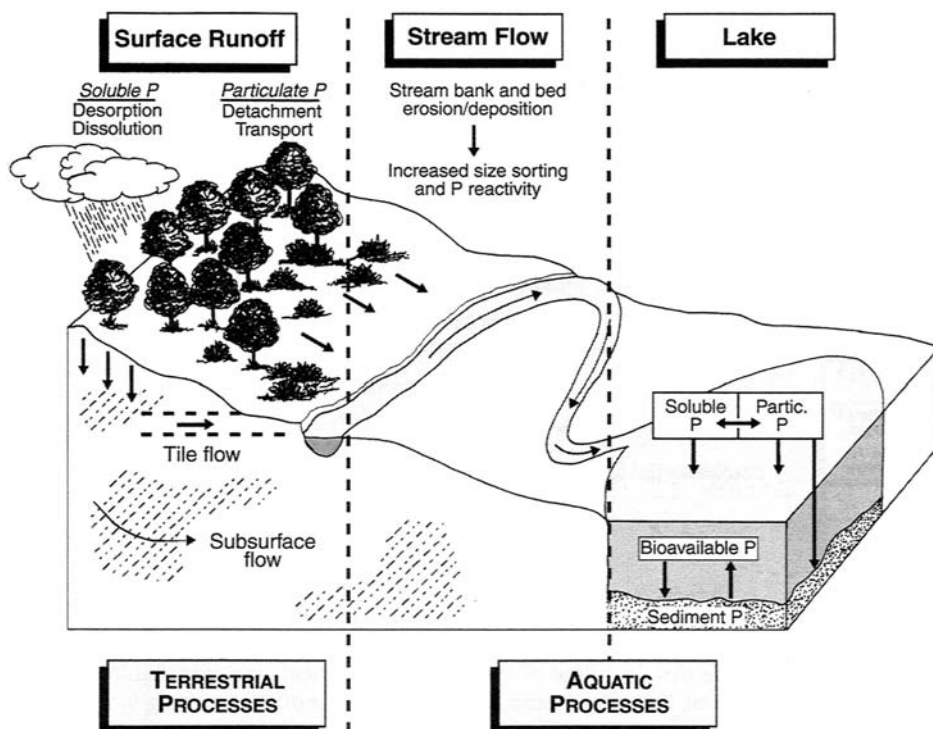


Figure 6.7 Phosphorus transport and fate in terrestrial and aquatic ecosystems. (Adapted from Sharpley, A. N. and A. D. Halvorson, in *Soil Processes and Water Quality*, R. Lal, Ed., Advances in Soil Science, Lewis Publishers, Boca Raton, FL, 1994.)

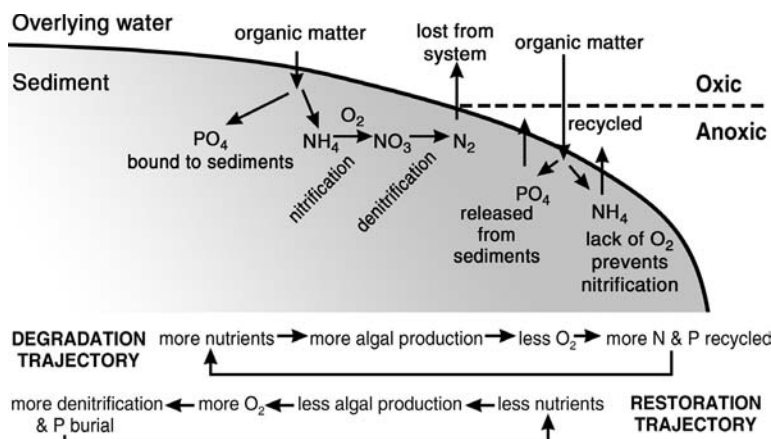


Figure 6.8 Overview of the degradation and restoration trajectories for the Chesapeake Bay, illustrating the relationships between nutrient loading, bottom sediments, and the O_2 status of waters overlying the sediments. (From Boesch, D. F. et al., *J. Environ. Qual.*, 30, 303–320, 2001. With permission.)

6.2 THE SOIL PHOSPHORUS CYCLE

Adequate P levels in soils are essential to produce agricultural crops, revegetate disturbed lands, and to grow plants for aesthetic or recreational purposes. Phosphorus fertilization is thus vital to modern agriculture. Phosphorus, found in all terrestrial environments, primarily originates from the weathering of soil minerals and other more stable geological materials. As P is solubilized in soils

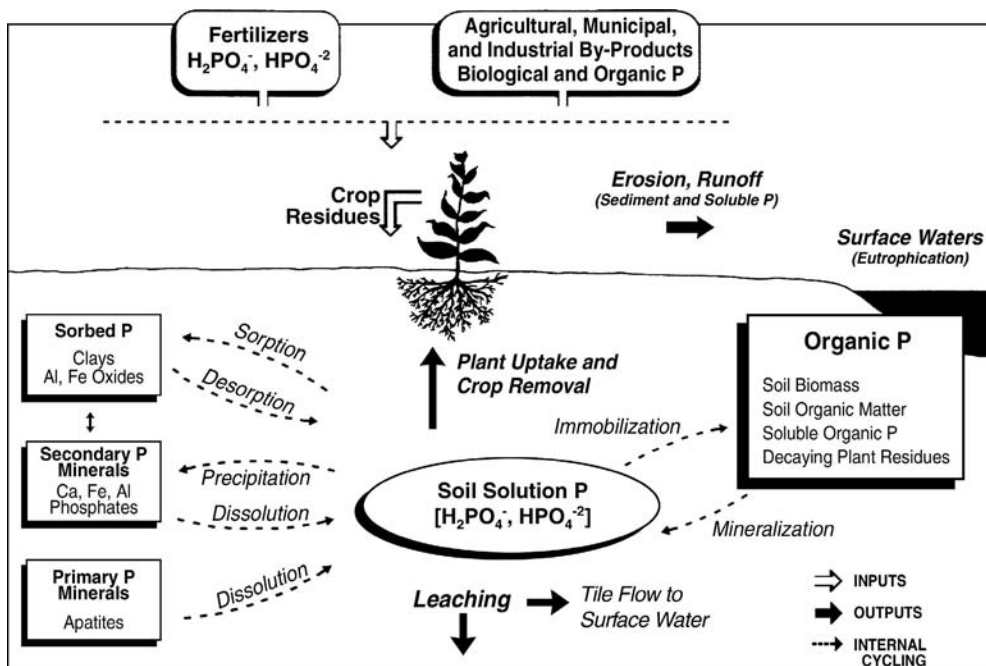


Figure 6.9 The soil P cycle. An overview of the physical, chemical, and microbiological processes controlling the availability of P to plants and P transport in runoff or leaching waters. (Adapted from Gachon, 1969.)

by the chemical and physical processes of weathering, it is accumulated by plants and animals, reverts to stable inorganic forms in the landscape, or is eroded from soils and deposited as sediments in freshwaters, estuaries, or oceans. Urban areas or large animal production operations convert biologically accumulated P (food or feed) into human or animal by-products (biosolids, manures) and recycle this P into the ecosphere with varying degrees of efficiency. Soil factors that control the rate of conversion of P between the inorganic and organic forms regulate the short- and long-term fates of P in the environment. The soil P cycle is a conceptual description of the chemical and microbiological reactions undergone by P in soils (Figure 6.9). Understanding how these reactions are influenced by natural and anthropogenic factors is essential to our efforts to improve agricultural productivity, manage urban lands, and protect or restore water quality and ecosystem health.

6.2.1 Inorganic Soil Phosphorus

Total P concentrations in soils range from 50 to 3000 mg/kg, with 50 to 70% in the inorganic form in mineral soils. In organic soils (>20 to 30% organic matter) from 60 to 90% of total P can be in organic forms. More than 150 mineral forms of P exist in the lithosphere, varying widely in solubility and thus in their ability to provide bioavailable forms of P. The minerals that weather and release P into the soil solution differ between soils, as a function of time and soil development (Figure 6.10a). In unweathered or moderately weathered soils, the dominant minerals are the apatites — calcium (Ca) phosphates with the general formula $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where X represents anions such as F^- , Cl^- , OH^- , or CO_3^{2-} . In areas of intense weathering, Ca and other basic minerals eventually leach from soils, pH decreases, and iron (Fe) and aluminum (Al) dissolve from mineral phases. Precipitates of Fe, Al, and P then form and become the main mineral forms of P in highly weathered soils. Amorphous oxides of Fe and Al are also common in highly weathered soils and act as “sinks and sources” for P, through a variety of chemical reactions collectively referred to as sorption and desorption (see Section 6.3.2).

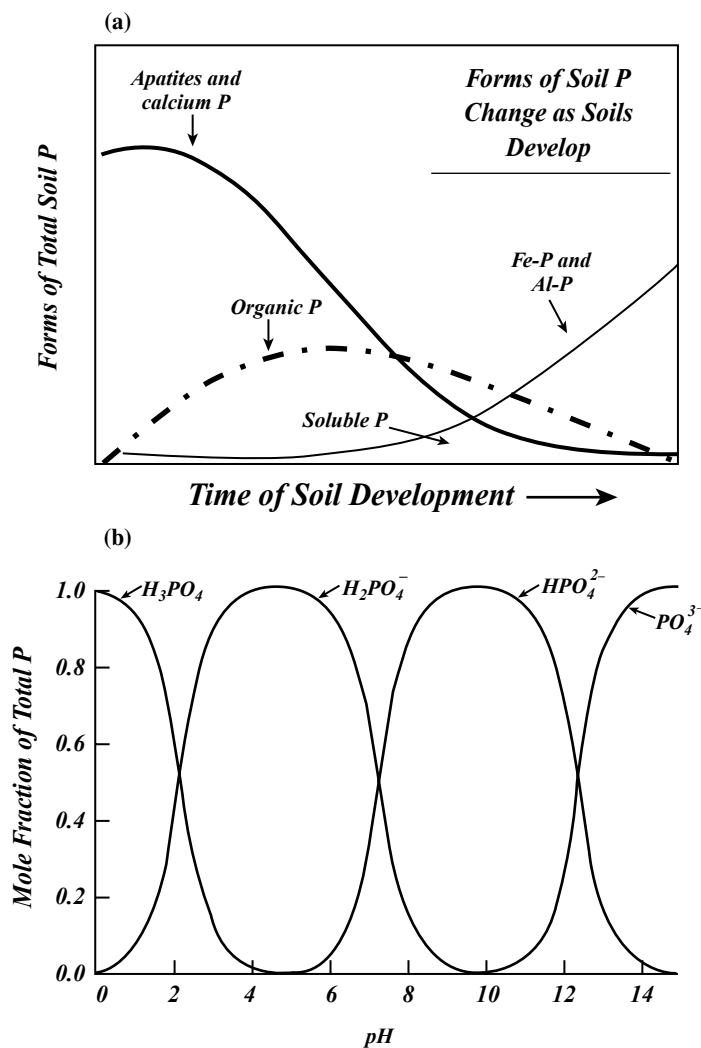


Figure 6.10 Changes in the form of soil P. (a) As affected by time and soil development for total P. (Adapted from Foth et al., 1997.) (b) As affected by soil pH for soluble P.

Example Problem 6.2

Laboratory analysis shows the total P concentration in the A horizon of an agricultural soil (0 to 15 cm) is 1500 mg P/kg. How many pounds of total P are there in an acre of this soil (assume that there are 2 million lb of soil in an acre to a depth of 6 in., ~15 cm)?

$$\text{Total P} = \frac{1500 \text{ mg P}}{\text{kg soil}} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{2.2 \text{ lbs P}}{\text{kg P}} \times \frac{1 \text{ kg soil}}{2.2 \text{ lb soil}} \times \frac{2 \times 10^6 \text{ lb soil}}{\text{acre}} = \frac{3000 \text{ lb P}}{\text{acre}}$$

This mixing of English and metric units would not be permissible in the SI system. Unfortunately, the SI system is not universally used and unit systems are still mixed in some areas of soil science. As a rule of thumb, the concentration of a substance in 6 in. of soil multiplied by 2 equals lb/acre. A typical bulk density is assumed in this rule of thumb. Coincidentally, in the metric system the concentration of substance in 15 cm of soil multiplied by 2 equals kg/ha, the metric equivalent of lb/acre, as is shown below. This is because the conversions from acres to hectares and from pounds

to kilograms essentially cancel one another. Assuming a bulk density of 1350 kg/m^3 (1.35 g/cm^3) and a depth of 0.15 m (15 cm), the mass of soil in 1 ha would be

$$\frac{1350 \text{ kg}}{\text{m}^3} \times 0.15 \text{ m} \times \frac{10000 \text{ m}^2}{\text{ha}} = \frac{2,025,000 \text{ kg soil}}{\text{ha}}$$

And it immediately follows that

$$\frac{1500 \text{ mg P}}{\text{kg soil}} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{2,025,000 \text{ kg soil}}{\text{ha}} \equiv \frac{3000 \text{ kg P}}{\text{ha}}$$

As P is dissolved or desorbed from soil minerals and colloids, it enters the soil solution in the form of primary (PO_4^{3-}) or secondary (HPO_4^{2-} , $\text{H}_2\text{PO}_4^{2-}$) orthophosphates, varying in relative concentrations as a function of soil pH (Figure 6.10b). Most soils range in pH from 4.0 to 9.0. At pH 4.0 to 6.5, $\text{H}_2\text{PO}_4^{2-}$ predominates, whereas at pH > 7.5 , HPO_4^{2-} is the major species of orthophosphate. Both are readily available for plant uptake. One common characteristic of P in soils at all stages of weathering is the low solubility of P-bearing minerals. In most agricultural soils, the soil solution concentration of P ranges from <0.01 to 1 mg P/L (ppm), although concentrations as high as 6 to 8 mg P/L have been measured in recently fertilized soils. A value of 0.2 mg P/L is often reported as the soil solution P concentration needed to optimize plant growth, but P concentrations as low as 0.03 mg P/L have been adequate to produce high yields of some agronomic crops.

6.2.2 Organic Soil Phosphorus

Phosphorus dissolved from minerals enters the soil solution where biological accumulation by plants and the soil microbial biomass occurs. Plants vary widely in their P contents, with most agricultural crops containing from 0.1 to 0.5% P, much less than the concentrations of other major essential elements such as N and potassium (K) (2.0 to 4.0%). In agricultural situations some of the P accumulated by plants is removed from the soil as harvested grain or forage, and the remainder is returned to the soil as crop residues (Table 6.3). In urban horticulture and native ecosystems, where “harvesting” does not occur, all of the P accumulated is eventually recycled back into the soil as plants die or lose vegetative matter in response to normal biological development. One major environmental concern in urban areas, however, is the conversion of biologically incorporated P in private or industrial landscapes into by-product organic matter (leaves and lawn clippings) that must then be beneficially reused, or disposed of, by municipalities through landfills or large-scale composting operations. Similarly, human wastes represent a transformation of biologically accumulated P from food chain crops to potentially recyclable organic matter (biosolids). An agricultural analogy to this situation is concentrated animal-based agriculture (feedlots, dairy, swine, and poultry operations) where harvested organic P (grains, forages, and silage) is transformed into animal manure organic and inorganic P (as much as 60% of the P in some animal manures is inorganic P). With time, much of the organic P added in biosolids and manures is degraded by soil microorganisms and converted to soluble and inorganic forms of P (Table 6.4). Because organic by-products, in both urban and agricultural systems, are often continually applied to the same soils within a limited geographic area, the buildup of soil P to values of environmental concern often occurs. Finding economic means to reuse organic by-products as soil amendments without enhancing P losses to water is one of the most significant environmental issues related to soil P management today (see Chapter 8).

Common forms of organic P found in soils include inositol phosphates, phospholipids, phosphoglycerides, phosphate sugars, nucleic acids, and phosphonates. Until recently, it has been difficult to identify specific forms of organic P in soils and to assess their bioavailability. This has

Table 6.3 Phosphorus Concentrations and Removal in the Harvested Portion of Some Major Agricultural Crops

Crop Category	Phosphorus Concentration (%)	Crop Yield		Phosphorus Removal (kg P/ha)
Grains				
Corn	0.28	9.4 Mg/ha	(150 bu/ac)	26
Rice	0.24	4.0 Mg/ha	(80 bu/ac)	10
Soybeans	0.58	2.7 Mg/ha	(40 bu/ac)	12
Wheat	0.45	2.7 Mg/ha	(40 bu/ac)	12
Forages				
Alfalfa	0.25	13.4 Mg/ha	(6 tons/ac)	34
Bermudagrass	0.32	22.4 Mg/ha	(10 tons/ac)	71
Corn silage	0.06	67.2 Mg/ha	(30 tons/ac)	39
Red clover	0.25	9.0 Mg/ha	(4 tons/ac)	22
Tall fescue	0.44	9.0 Mg/ha	(4 tons/ac)	39
Specialty				
Beans, snap	0.06	26.9 Mg/ha	(12 tons/ac)	15
Celery	0.14	2470 crates/ha	(1000 crates/ac)	90
Onions	0.05	40.3 Mg/ha	(18 tons/ac)	19
Potatoes	0.04	448 quintals	(400 cwt.)	17
Sugar cane	0.02	224 Mg/ha	(100 tons/ac)	48
Sweet corn	0.07	6.7 Mg/ha	(3 tons/ac)	5
Tomatoes	0.04	67.2 Mg/ha	(30 tons/ac)	27

Source: Adapted from Pierzynski and Logan, 1993.

Table 6.4 Forms of P in Soils Amended with Organic Wastes

	Total P	Organic P (mg/kg)	Inorganic P (mg/kg)
Manure-Amended Soils (Sims, 1992)			
Four Delaware soils	1467	281 (19%)	1166 (81%)
Seven Pennsylvania soils	2240	427 (19%)	1813 (81%)
Pullman Clay Loam (Sharpley et al., 1984)			
Untreated soil	353	202 (57%)	151 (43%)
Soil + fertilizer P	457	231 (51%)	226 (49%)
Soil + feedlot waste at 67 Mg/ha/year	996	323 (32%)	673 (68%)
Greenfield Sandy Loam (Chang et al., 1983)			
Untreated soil	579	60 (10%)	519 (90%)
Soil + biosolids at 45 Mg/ha/year	1433	122 (9%)	1211 (91%)

changed due to the more widespread application of ^{31}P nuclear magnetic resonance spectroscopy (NMR) to the study of soil organic P. Using ^{31}P NMR, as shown in Figure 6.11, it is now possible to more precisely identify actual forms of organic P present in soils, their bioavailability (e.g., as assessed with the Olsen soil P test, 0.5 M NaHCO_3 at pH 8.5), and how they are related to soil physical and chemical properties. Data in Figure 6.11b show that bioavailable organic P will tend to accumulate in acidic soils with high clay contents and in cooler, drier climates. Causes for this

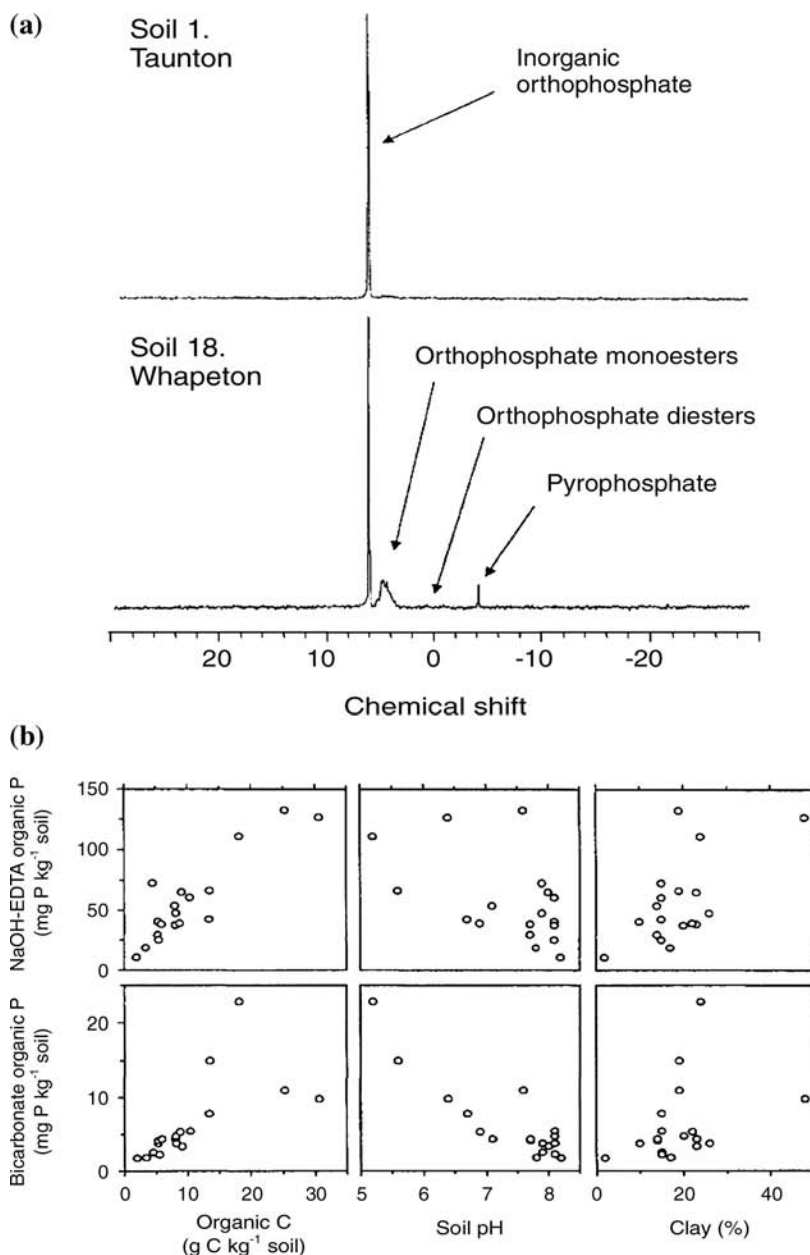


Figure 6.11 (a) Use of solution ^{31}P NMR spectra to identify P compounds present in two soils from the Western United States with low (Taunton) and high (Whapeton) organic C contents; (b) relationship between bioavailable organic P (bicarbonate organic P in the Olsen soil test P extract), organic P determined by NaOH-EDTA extraction and ^{31}P NMR, and selected soil properties. (From Turner, B. L. et al., *Soil Sci. Soc. Am. J.*, 67, 1168–1179, 2003. With permission.)

include physical protection of organic P compounds from microbial decomposition because of sorption of organic P to clay minerals; the fact that phosphate esters are more chemically stable at lower pH values; and reduced microbial activity in acid soils, at lower temperatures, and under moisture-limited conditions (Turner et al., 2003).

Microbial decomposition of organic P results in the release of soluble organic P that, with time, is normally converted into stable inorganic forms of P. Studies have shown, however, that as much as 50% of the P transported in runoff can be soluble organic P. The extent and rate of conversion of organic P into soluble or stable inorganic forms is highly dependent on the nature of the original organic material, as well as environmental factors such as pH, temperature, and soil moisture. Fresh plant residues may quickly release P into the soil solution while more stable forms of organic matter, such as soil humus, animal manures, municipal biosolids, or composts, generally act as long-term, slow-release sources of P. Mineralization, the conversion of organic P to inorganic P, usually occurs rapidly if the carbon (C):P ratio of the organic matter is <200:1, while immobilization, the incorporation of P into microbial biomass, occurs if C:P ratios are >300:1. At this time, it is unclear whether plants can directly absorb soluble organic P or whether enzymatic action is required to cleave orthophosphate molecules from organic compounds prior to uptake by plant roots.

6.2.3 Phosphorus Additions to Soils

The low solubility of P in many soils indicates that the soil solution must be replenished frequently and rapidly with soluble P if adequate plant growth is to occur. In soils with high P fertility levels, the soil alone can normally provide all P required by most plants. The need for additional P can be determined by soil testing (see Chapters 4 and 8) and inorganic or organic P sources, such as commercial fertilizers, manures, biosolids, or even industrial by-products, can be added to soils to ensure that P deficiency does not limit plant growth.

Commercial P fertilizers are produced by industrial processes that react phosphate ores (e.g., fluorapatite, or “rock phosphate”) with sulfuric acid (ordinary superphosphate, 9% P), phosphoric acid (triple superphosphate, 20 to 22% P), or phosphoric acid with ammonia (mono-ammonium phosphate, 21% P; diammonium phosphate, 23% P). Rock phosphate (13 to 17% P) can also be used directly as a P fertilizer, although its low solubility, particularly in calcareous soils, often means high application rates are needed to provide sufficient available P for optimum yields. Situations where rock phosphate is most effective include highly weathered, acid soils with low Ca contents, soil conditions that promote the dissolution of apatite minerals (rock phosphate). The P content of the most commonly used inorganic and organic sources of P is provided in Table 6.5.

Animal manures, municipal biosolids, or composts applied to agricultural lands, as part of efforts to reuse (or dispose of) these by-products beneficially, contain relatively low concentrations of P (0.1 to 3.0%) compared to commercial fertilizers. Most also contain an unfavorable N:P ratio relative to many crops, resulting in the overapplication of P when these organic P sources are applied to meet crop N requirements, the long-standing practice in most agricultural settings. This is exacerbated by the relatively small amounts of P actually removed from the soil in harvested grain or forage (Table 6.3; Figure 6.12). With time, these overapplications can lead to increased risks of P loss to waters by surface and subsurface flow. Unfortunately, because of transportation and handling costs, most animal-based agricultural operations have few alternatives to land application of manures within a short distance from the area where the animals are grown. If these overfertilized soils are near a sensitive water body, the potential environmental impacts of increasing soil P values above agronomic optimum concentrations can become a socioeconomic and political issue. Similarly, for municipalities, the alternatives to land application of organic by-products (mainly landfills and incineration) are increasingly limited, costly, and may have more serious environmental impacts than well-managed land application programs. Some solutions to the P management problems faced by animal agriculture are emerging, such as the use of improved, modified diets

Table 6.5 Major Inorganic and Organic Sources of P for Crop Production

Phosphorus Source and Chemical Composition		P (%)	P ₂ O ₅ (%)	Other Nutrients
Commercial Fertilizers				
Ordinary superphosphate	[Ca(H ₂ PO ₄) ₂ + CaSO ₄]	7–10	16–23	Ca, S (8–10%)
Triple superphosphate	[Ca(H ₂ PO ₄) ₂]	19–23	44–52	Ca
Monoammonium phosphate (MAP)	[NH ₄ H ₂ PO ₄]	26	61	N (12%)
Diammonium phosphate (DAP)	[(NH ₄) ₂ HPO ₄]	23	53	N (21%)
Urea-ammonium phosphate	[CO(NH ₂) ₂ + NH ₄ H ₂ PO ₄]	12	28	N (28%)
Ammonium polyphosphates (liquid)	[(NH ₄) ₃ HP ₂ O ₇]	15	34	N (11%)
Rock Phosphates				
United States (Florida)	Ca ₁₀ F ₂ (PO ₄) ₆ ·XCaCO ₃ (varies between mineral deposits)	14	33	Major impurities: Al, Fe, Si, F, CO ₃ ²⁻
Brazil		15	35	
Morocco		14	33	
Former U.S.S.R.		17	39	
Organic Phosphorus Sources				
Beef manure		0.9	2.1	N, K, S, Ca, Mg, and trace elements
Dairy manure		0.6	1.4	
Poultry manure		1.8	4.1	
Swine manure		1.5	3.5	
Aerobically digested sludge		3.3	7.6	
Anaerobically digested sludge		3.6	8.3	
Composted sludge		1.3	3.0	

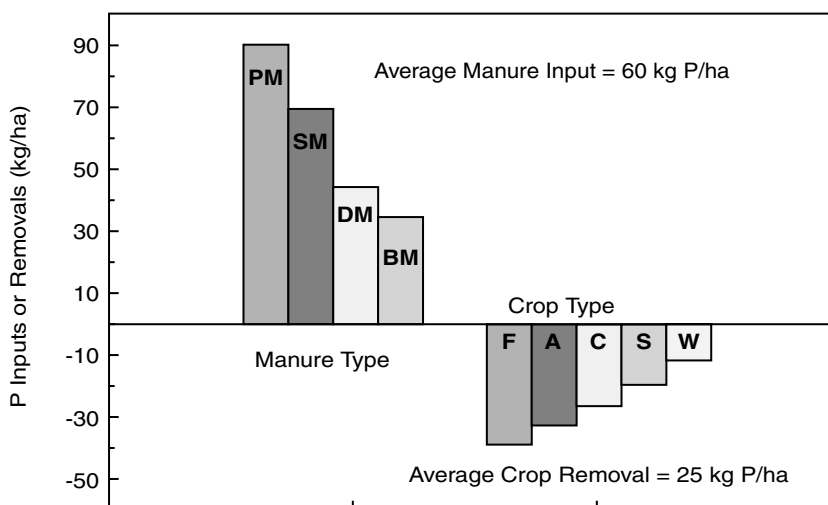


Figure 6.12 Comparison of typical inputs of P from animal manures and crop removal in harvested grain or forage (PM = poultry manure, SM = swine manure, DM = dairy manure, BM = beef manure; F = fescue, A = alfalfa, C = corn, S = soybeans, and W = wheat).

Table 6.6 (A) Effect of Modifying Swine Diets with Phytase Enzymes and Low Phytic Acid (high available P or HAP) Corn on P Content in Swine Manure (g P/kg dry matter) and (B) Reducing Overfeeding of Mineral P Concentrates to Dairy Cows on Total, Soluble, and Bioavailable P in Dairy Manure (g P/kg dry matter)

A						
Diet	TP	DRP	DOP	ASRP	ASOP	PAP
Control	25.5	11.9	1.1	23.5	1.8	3.9
PHY	21.2	11.7	1.0	17.5	1.4	2.0
HAP	20.7	10.8	1.0	16.6	1.0	1.6
HAP + PHY	15.2	7.9	0.9	11.7	1.2	0.7
B						
Diet	TP	WSP	BAP			
High P	8.9	3.7	6.1			
Low P	4.9	1.4	2.1			

Note: TP = total P; DRP = dissolved reactive P; DOP = dissolved organic P; ASRP = acid-soluble reactive P; ASOP = acid-soluble organic P; PAP = phytic acid P; WSP = water-soluble P; BAP = bioavailable P.

Sources: A, adapted from Baxter et al., 2003; B, adapted from Ebeling et al., 2002.

that can reduce P excretion by most animal species. For example, a swine diet that included phytase enzymes and low phytic acid corn significantly reduced the amount of total P, soluble P, and all P fractions in swine manure. Reducing overfeeding mineral concentrate forms of P to dairy cows decreased total, soluble, and bioavailable P in dairy manures (Table 6.6).

Example Problem 6.3

A poultry manure sample is tested for N and P and found to contain 4.0% total N and 2.0% total P. Corn grain grown using this manure has a total N content of 1.5% and a total P content of 0.27%.

What are the N:P ratios of the poultry manure and corn grain? If 8 Mg/ha of manure are applied and

7000 kg/ha of grain are harvested, how much manure P is (a) removed in harvested grain; (b) remains in the soil, in units of kg P/ha?

$$\text{Manure N:P ratio} = \frac{4.0\% \text{ total N}}{2.0\% \text{ total P}} = 2.0$$

$$\text{Corn grain N:P ratio} = \frac{1.5\% \text{ total N}}{0.27\% \text{ total P}} = 5.56$$

$$\text{Total manure P added} = \frac{8 \text{ Mg}}{\text{ha}} \times \frac{1000 \text{ kg}}{\text{Mg}} \times \frac{0.02 \text{ kg P}}{\text{kg manure}} = \frac{160 \text{ kg P}}{\text{ha}}$$

$$\text{P removed in corn grain} = \frac{7000 \text{ kg grain}}{\text{ha}} \times \frac{0.0027 \text{ kg P}}{\text{kg grain}} \cong \frac{19 \text{ kg P}}{\text{ha}}$$

$$\text{P remaining in soil} = \frac{160 \text{ kg P}}{\text{ha}} - \frac{19 \text{ kg P}}{\text{ha}} = \frac{141 \text{ kg P}}{\text{ha}}$$

The addition of metal salts (e.g., alum, ferric chloride) to some manures or biosolids can reduce P solubility in these by-products which, in turn, decreases the potential for dissolved P losses by overland flow and leaching. For example, as shown in Figure 6.13a adding alum to poultry litters (mixtures of manure and sawdust or woodchips used for bedding in poultry houses) has been shown to be an effective means to decrease dissolved P losses in overland flow. In much of the southeastern United States, poultry litters are applied to pastures as a fertilizer. In this situation the application of animal manure not only contributes to the long-term buildup of soil P, but also represents a direct source of dissolved P loss in overland flow, as the litters are not incorporated with the soil, but remain on the surface of the pasture. About 20% of the total P in most poultry litters is water soluble; hence, rainfall events can release soluble P directly from the litters and transport this P to surface waters in runoff, where it is immediately available to algae. Research has shown that alum, which is also used to remove soluble P from municipal wastewaters, could be applied to the litters in the poultry houses after the poultry were removed for processing. Alum reduced the solubility of P in the litters, thus decreasing the risk of P loss in runoff. Other benefits resulted from this BMP. The acidifying nature of alum decreased ammonia levels in the poultry houses, improving poultry performance and profitability and decreasing ammonia emissions (an air quality benefit), and also decreased runoff losses of soluble organic C and some trace elements.

Adding alum or FeSO_4 to municipal wastewaters to remove P prior to discharging treated waters to rivers or streams also affects P solubility in the biosolids that are by-products of wastewater treatment. As shown in Figure 6.13b, soils amended with biosolids #1, high in Fe (54%) and Al (16%), had a lower concentration of soluble P (KCl-P) and a lower percentage of added total P leached than biosolids #2, low in Fe (7%) and Al (7%), or poultry manure and fertilizer P (triple superphosphate). The importance of soil properties in mitigating P leaching is also clearly shown in this figure, where the percentage of P leached was consistently lower for the Candler soil (moderate P sorption capacity) than the Immokalee soil (low P sorption capacity). It is important to remember that, because treating manures and wastewaters with metal salts does not reduce their total P concentration, erosion control practices that prevent the loss of particulate P from soils receiving these by-products is essential. Also adding these, or any P source, to soils at rates greater than crop P removal will continually increase soil P values and should be avoided if at all possible.

Inorganic by-products from industrial operations, such as basic slag (3 to 5% P), a steel manufacturing by-product, or coal ash (<1% P), a by-product of the electric power industry, are

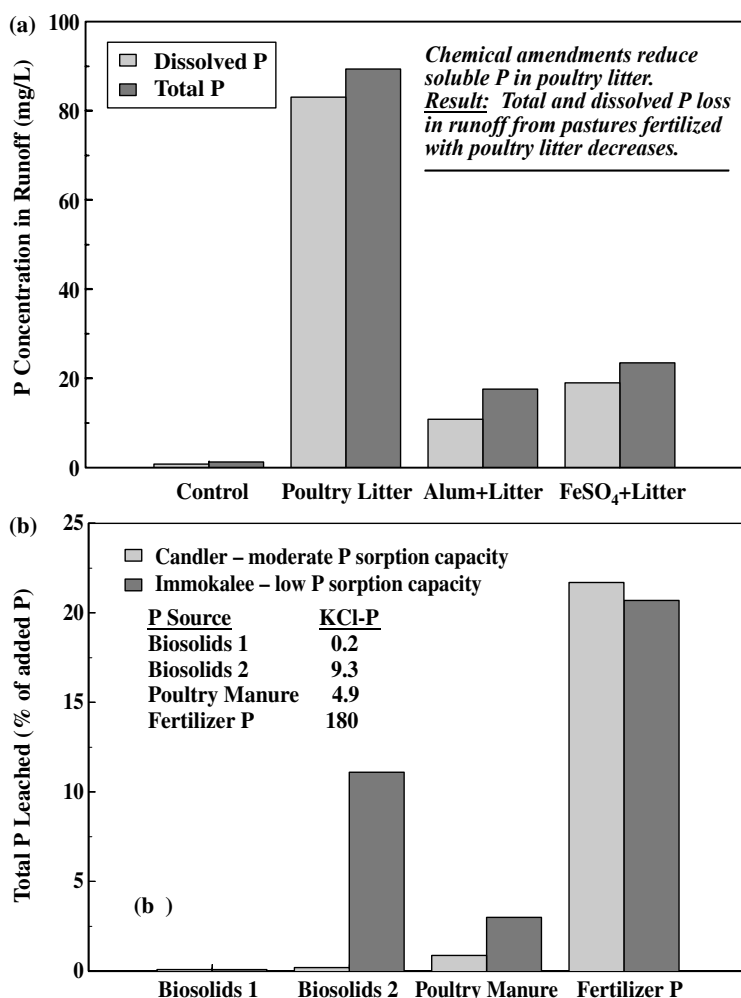


Figure 6.13 (a) Effect of amending poultry litters with metal salts (alum or FeSO₄) on dissolved and total P concentrations in runoff from fescue pastures. (Adapted from Shreve, B.R. et al., 1995.) (b) Effect of biosolids type (biosolids #1: high Fe and Al content; biosolids #2: low Fe and Al content) and soil P sorption capacity on the percentage of P leached from two Florida soils, relative to poultry manure and fertilizer P. (Adapted from Elliott et al., 2002.)

other, relatively inexpensive sources of P. While the solubility and thus plant availability of P in industrial by-products is less than fertilizers and animal manures, land application is an economically desirable alternative to landfill disposal of these by-products. Management programs that use these materials as soil amendments must also consider the effects on soil pH, soluble salts, the presence of potentially phytotoxic elements, e.g., boron (B), sodium (Na), and the long-term fate of nonessential heavy metals found in these by-products.

6.3 PHOSPHORUS TRANSFORMATIONS IN SOILS

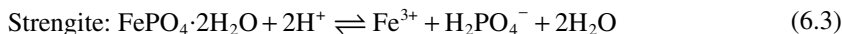
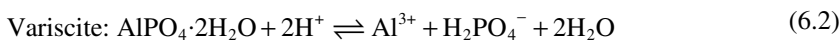
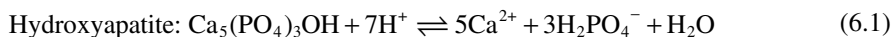
The dual goals of soil P management are to maintain the concentration of biologically available soil P at a value adequate for plant growth, while minimizing the movement of dissolved and particulate P to surface waters and shallow groundwaters. Soil, plant, and water management practices, such as fertilization techniques and timing, manure and biosolids management

practices, crop rotation, tillage, irrigation, drainage, terracing, grassed waterways, and buffer strips, all act to maximize P recovery from fertilizers and organic by-products and reduce P transport from land to water. These BMPs represent practical applications of the basic knowledge gained from our understanding of the soil P cycle and are discussed in detail in Chapter 8. For crop production purposes, these practices focus on maintaining concentrations of bioavailable P in soils in the range considered optimum for plant growth, and on minimizing soil loss to prevent long-term degradation of the soil resource and thus soil productivity. Although similar in many respects to agricultural BMPs, environmental BMPs for P must be more intensive and have less room for error due to the very small P losses from soils required to induce eutrophication. In either case, basic knowledge of the chemical, microbiological, and physical transformations of soil P is needed to develop innovative approaches that meet both agronomic and environmental goals.

The major soil inorganic P transformations are the fixation of P in sparingly soluble forms by *precipitation* and *sorption* reactions and the solubilization of P by mineral *dissolution* and *desorption* reactions. Soil organic P transformations are primarily *mineralization-immobilization* reactions mediated by soil microorganisms and P uptake by plant roots alone or in association with mycorrhizal fungi.

6.3.1 Mineral Equilibria: Dissolution and Precipitation of Soil Phosphorus

The weathering of primary minerals containing P slowly releases orthophosphate into the soil solution where it can be absorbed by plants and microorganisms. The major primary P minerals in soils are reasonably well known. In soils that have not been extensively weathered, P mineralogy is dominated by sparingly soluble apatites (e.g., hydroxyapatite, $\text{Ca}_5\text{OH}(\text{PO}_4)_3$) and other more-soluble calcium phosphates — octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), monetite (CaHPO_4), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). As soils weather, apatites dissolve, Ca^{2+} is lost by leaching or crop uptake, and Al or Fe forms of P become more important. In highly weathered, acidic soils, Al phosphates — berlinite (AlPO_4), variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), tarakanite ($\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$) — and Fe phosphates — strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), tenticite ($\text{Fe}_6(\text{PO}_4)_4(\text{OH})_6 \cdot 7\text{H}_2\text{O}$), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) — predominate. The theoretical equilibrium reactions for most P minerals have been determined, such as



Predicting soil solution concentrations of P with mineral equilibrium reactions such as these has met with mixed success. Reasons include the complex, uncertain nature of solid phases of soil P; the unpredictable, often very slow rates of mineral dissolution; and the fact that true equilibrium is rare in soils due to losses of P by plant uptake, leaching, runoff and additions of P in fertilizers, manures, and by microbial decomposition of organic matter. For a review of the principles and limitations of mineral equilibria as a method to assess soil P availability, see Lindsay and co-workers (1979, 1989).

Secondary minerals can also form in soils by precipitation from saturated soil solutions that exceed the solubility product of a mineral. Precipitation is defined as the formation of discrete, insoluble compounds in soils, and can be viewed as the reverse of mineral dissolution. The most common secondary P minerals are the products of reactions between soluble P and Ca, Al, or Fe. In neutral or calcareous soils, where the pH is higher and soluble Ca is the dominant cation, the addition of soluble P in fertilizers, manures, or by mineralization of organic residues initially results in the formation of dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), which, with time, slowly reverts to other more-stable Ca phosphates such as octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), and in the long term to apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). In acidic soils, where Al and Fe are the major soluble cations, Fe and Al phosphates are the dominant precipitates. The presence of amorphous or partially crystalline Fe and Al oxides that can sorb or occlude P as they crystallize in acid soils makes identification of specific Fe-P and Al-P minerals difficult.

The solubility of primary and secondary P minerals is controlled by soil pH, soil solution concentrations of Al, Fe, Ca, magnesium (Mg), and other soil properties such as the oxidation–reduction (redox) status of the soil, temperature, and moisture. Dissolution of P minerals in calcareous and acidic soils is highly pH dependent. In general, the solubility of P-bearing minerals, and thus the availability of P to plants (and runoff or leaching waters), is greatest under slightly acidic conditions (pH 6.0 to 6.5).

6.3.2 Sorption and Desorption of Soil Phosphorus

The principles and mechanisms for sorption and desorption of anions (e.g., phosphate, sulfate, nitrate) by soils are discussed in Chapter 3. For P, *sorption* reactions commonly include nonspecific adsorption (anion exchange); and chemisorption (ligand exchange), the formation of a chemical bond between a phosphate anion (e.g., H_2PO_4^- , HPO_4^{2-}) and a soil colloid (Figure 6.14a). Desorption is release of P from a solid phase into the soil solution by processes other than mineral dissolution. *Desorption* occurs when plant uptake, runoff, or leaching depletes soil solution P concentrations to very low levels, or in aquatic systems when sediment-bound P interacts with low P waters. Only a small fraction of sorbed P in most soils is readily desorbable. Most P added to soils in fertilizers or manures is rapidly sorbed but not easily desorbed, a phenomenon called *hysteresis* (Figure 6.14b). Hysteresis can be due to surface precipitation of P, occlusion of P by other precipitates, and slow diffusion of P into the interior of a soil solid.

Phosphorus sorption reactions are kinetically biphasic; that is, they have a rapid initial reaction, typically 1 day or less, followed by a slow reaction that can last for weeks or longer. For sorption, the initial reaction represents nonspecific adsorption and ligand exchange on mineral edges or by amorphous oxides and carbonates. The slow reaction involves surface precipitation or polymerization on mineral surfaces or diffusion of adsorbed P into the interior of solid phases. The time-dependent nature of P sorption is shown in Figure 6.15a, for acidic Irish soils varying in amorphous Al and Fe. Desorption of P is also temporally biphasic (Figure 6.15b). The “fast desorbing pool” represents P bound to reactive surfaces in direct contact with the aqueous phase, soluble P released from unstable solid phases formed from recent additions of fertilizer or manure, physically adsorbed orthophosphate, and P complexed by organic matter. Soil P in the “slow desorbing pool” likely originates from diffusion of P from the interior of soil solid phases or aggregates or slow dissolution of amorphous or crystalline solid phases of P.

The major factors that influence P sorption and desorption by soils and sediments are similar to those described for other anions in Chapter 3. In general, soils that are low in P, acidic, and high in clay or Fe/Al oxides, particularly amorphous oxides, have the greatest P sorption capacities. Sorption of P generally decreases as soil pH increases because functional groups on the surface of clays and metal oxides become deprotonated (e.g., $\text{OH}_2^+ \rightarrow \text{OH}_2 \rightarrow \text{OH}^-$); thus, the colloidal surface

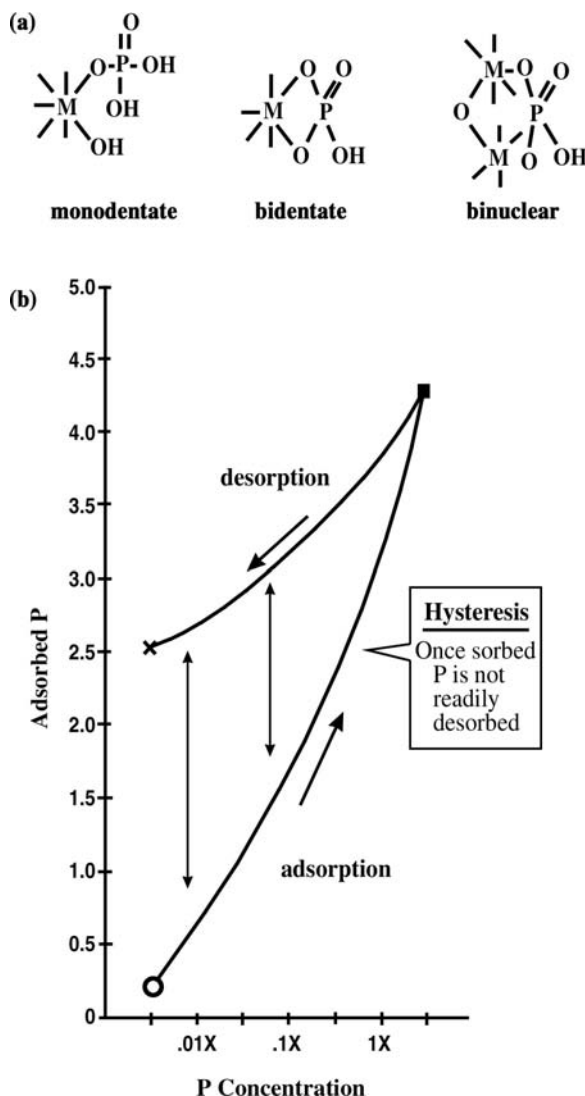


Figure 6.14 Phosphorus sorption and desorption processes in soils. (a) Proposed mechanisms of adsorption of P by soil constituents, M represents a metal (Fe, Al) ion in a clay or oxide. (b) Idealized sorption-desorption curve for P, illustrating hysteresis. When P is added to the soil, as in fertilization, and the concentration of P in the soil solution (x) increases (e.g., from 0.01 to 1 times), sorbed P increases as well. However, there is a lack of complete reversibility in desorption of P from the solid phase, referred to as hysteresis, when the concentration of P in the soil solution decreases from 1 to 0.01 times by processes such as plant uptake, leaching, or runoff. (From Fixen, P. E. and J. H. Grove, in *Soil Testing and Plant Analysis*, R. L. Westerman, Ed., American Society of Agronomy, Madison, WI, 141–180, 1990. With permission.)

becomes progressively more negatively charged. The effect of clay content is clearly seen in Figure 6.16 where the amount of P sorption that must occur to attain a P concentration in solution adequate for plant growth (~0.2 mg/L) would be ~2500 mg P/kg for a Hawaiian Inceptisol (70% clay), compared with ~50 mg P/kg for a Peruvian Ultisol (6% clay). In calcareous soils, CaCO_3 and Fe oxides are the main factors controlling P sorption.

Sorption also varies with soil depth and is affected by cultural operations that alter soil P levels, soil pH, and organic matter content, such as fertilization, liming, manuring, or reduced tillage operations. Therefore, when assessing the practical implications of P sorption to crop production

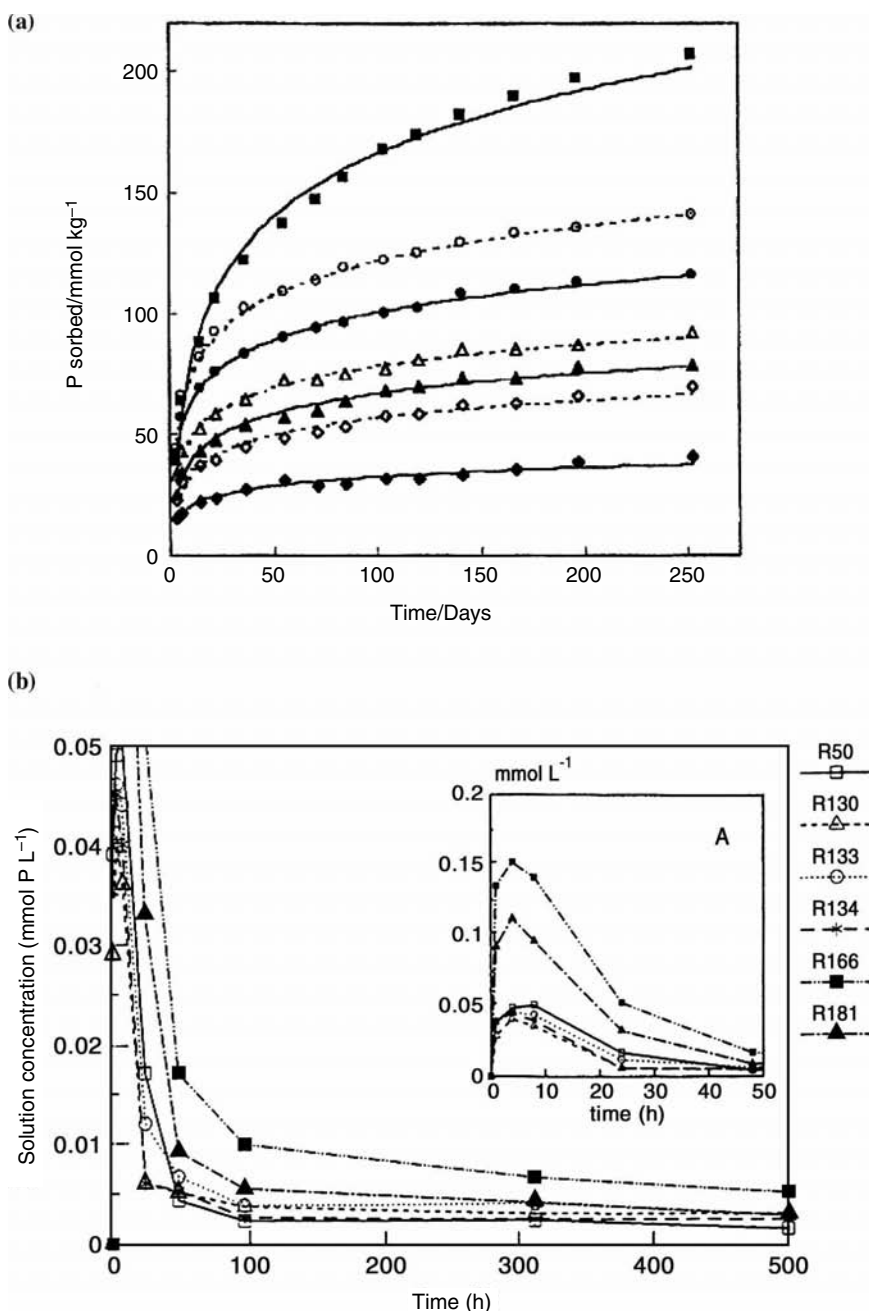


Figure 6.15 (a) Illustration of fast and slow sorption of P by seven Irish soils. (From Maguire, R. O. et al., *Eur. J. Soil Sci.*, 52, 479–487, 2001. With permission.) (b) Short and long-term kinetics of P desorption from six Belgian soils. (From Freese, D. et al., *Soil Sci. Soc. Am. J.*, 59, 1295–1300, 1995. With permission.)

and water quality, it is important to consider soil management and the entire soil profile. Phosphorus availability is usually enhanced by liming acid soils because this decreases sorption of P and the potential for precipitation of Al and Fe secondary P minerals. However, overliming acid soils can reduce P availability by favoring the precipitation of solid phases of Ca-P. Organic matter additions

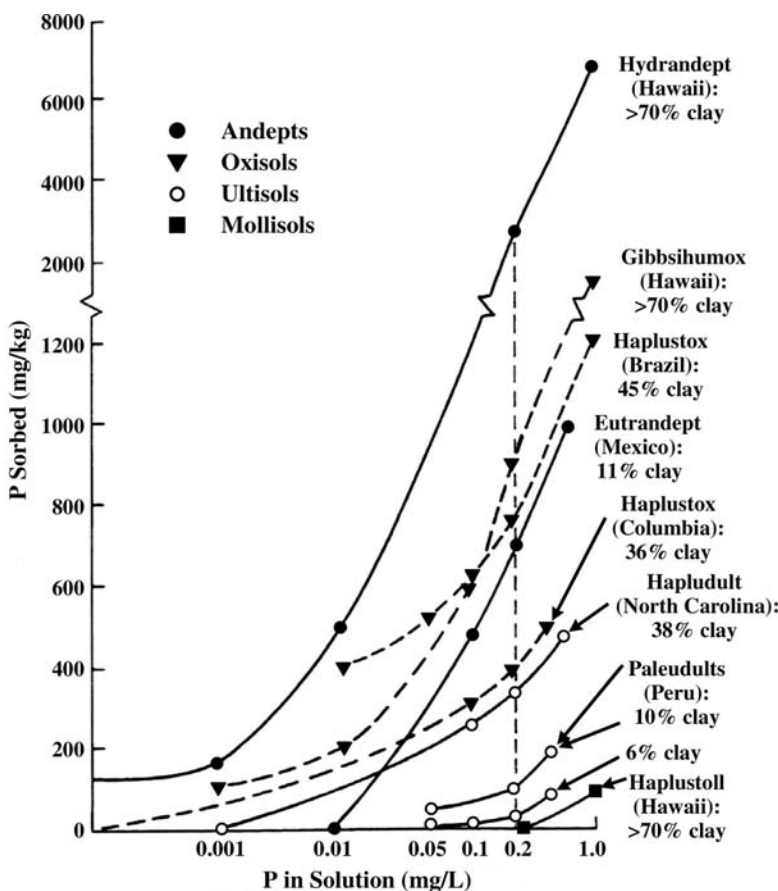


Figure 6.16 Differences in P sorption capacity of soils from four soil groups. Vertical dashed line represents the amount of P that must be sorbed to attain a level in solution adequate for the growth of most crops (0.2 mg/L). (From Sanchez, P. A. and G. Uehara, in *The Role of Phosphorus in Agriculture*, F. E. Khasawneh, Ed., American Society of Agronomy, Madison, WI, 471–514, 1980. With permission.)

(manures, crop residues) can reduce P sorption because large humic acid molecules can sorb to the surfaces of clays and oxides, blocking P sorption sites; also, organic anions released by microbial decomposition of organic matter compete directly with P in sorption reactions. Flooding and draining soils can cause changes in pH, dissolve Fe-P minerals, and alter the crystallinity and surface properties of Fe oxides, all of which can affect P sorption.

The role of subsoils in P sorption and leaching is shown in Figure 6.17. The Evesboro soil, with sandy surface and subsoil horizons, has much less overall sorption capacity in the soil profile than the Matawan sandy loam, which has a subsoil horizon with 60% clay. The higher soil test P (STP) values in the Evesboro subsoil reflect the greater mobility of P in profiles with little accumulation of clay. Tillage practices that affect the vertical distribution of P in the soil profile can also alter sorption and desorption of P. No-tillage agriculture, where P and crop residues are not incorporated by plowing, often results in stratification of P and organic matter, with extremely high values for both soil properties in the top few centimeters of the soil. This can result not only in a lower P sorption capacity in this depth (0 to 2 cm), but also in very high levels of easily extractable P relative to the remainder of the topsoil (6 to 18 cm), a situation that could contribute to higher levels of dissolved P in runoff (Figure 6.18).

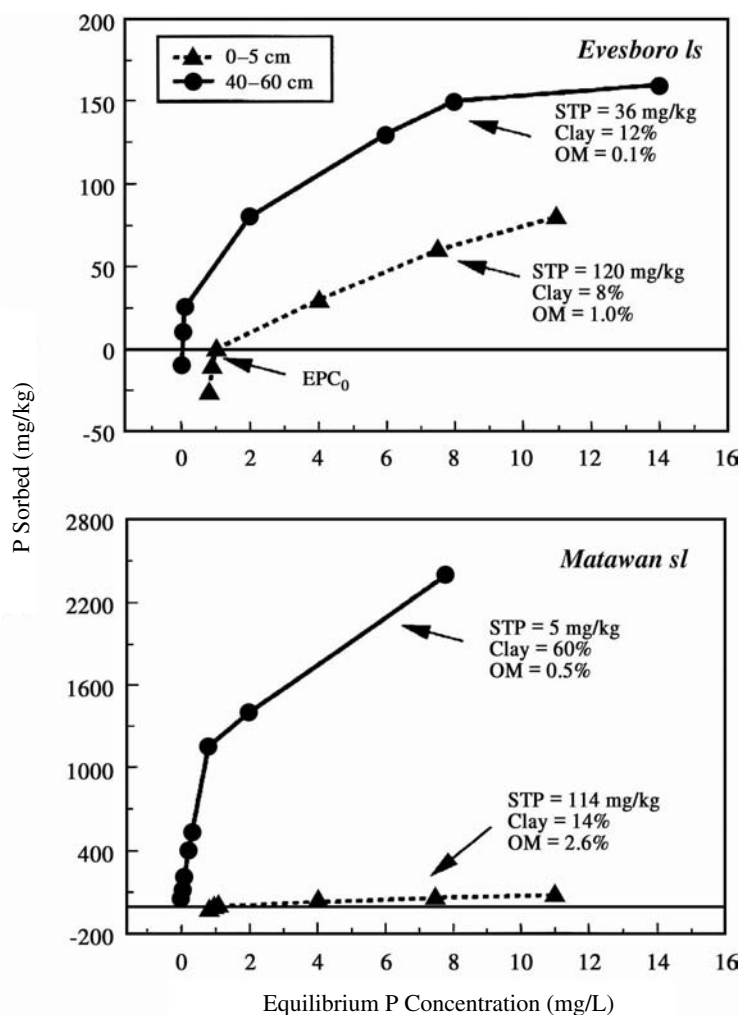


Figure 6.17 Phosphorus sorption isotherms for two depths of two Atlantic Coastal Plain soils. The 0 to 5 cm depth represents the zone of maximum interaction between runoff and soil P, and the 40 to 60 cm depth represents the potential for subsoils to retain P against leaching. STP refers to soil test P value prior to sorption (soil test = Mehlich 1, 0.05 M HCl + 0.0125 M H₂SO₄). EPC₀ is equilibrium concentration of P in solution when the rates of P sorption and desorption are the same. (Adapted from Mozaffari and Sims, 1994.)

Models to quantify sorption and desorption of P (e.g., Langmuir and Freundlich isotherms) are described in Chapter 3. A particularly useful parameter derived from P sorption isotherms is the EPC₀ (equilibrium P concentration at zero sorption) value, defined as the solution P concentration maintained by a soil or sediment when rates of P sorption and desorption are equal. The EPC₀ values characterize the potential of soils or sediments in contact with runoff or surface waters to remove P from or release P into flowing waters. Soils or sediments with high EPC₀ values that interact with low P waters (rainfall, subsurface discharge) will desorb P; conversely, if EPC₀ values are low, soils or sediments will sorb P, reducing the P concentration of runoff or stream flow and decreasing the potential for eutrophication. The high EPC₀ values for the top few centimeters of the Evesboro soil in Figure 6.17 (~1 mg/L) and the Canfield soil (0–2 cm) in Figure 6.18 (~3 mg/L) indicate these soils should readily desorb soluble P into runoff waters.

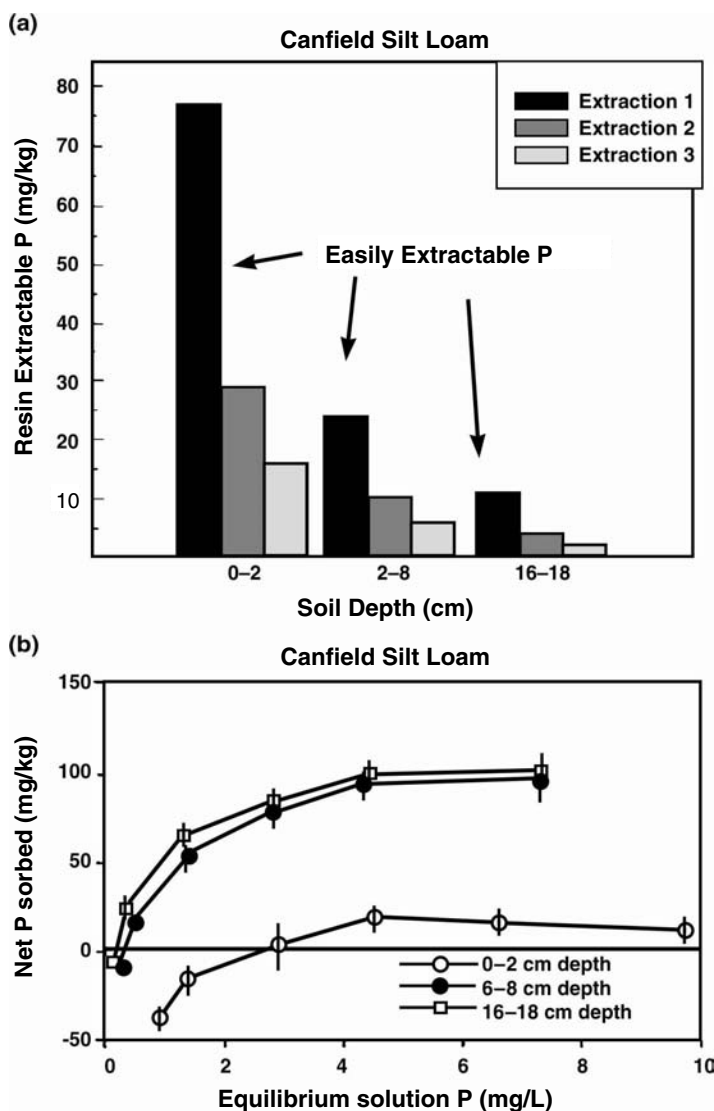


Figure 6.18 Comparison of easily extractable P and P sorption isotherms for the upper (a) and lower (b) portions of the surface horizon of a Canfield silt loam used for the production of no-till corn. (Adapted from Guertal, 1991.)

Rapid tests for P sorption, often referred to as P sorption indices (PSI) or single point P isotherms, have also been developed because P sorption isotherms are time-consuming and costly to conduct. The PSI tests typically involve overnight equilibration of a soil with one P solution with a very high P concentration (e.g., 1000 mg P/kg soil). As shown in Figure 6.19, PSI values are usually well correlated (a) with estimates of P sorption maxima derived from Langmuir isotherms and (b) with long-term P sorption. Thus, the PSI gives a rapid, inexpensive assessment of the effects of soil properties and soil management on P sorption for large numbers of soil samples and can increase the practical use of P sorption information in a variety of land application programs.

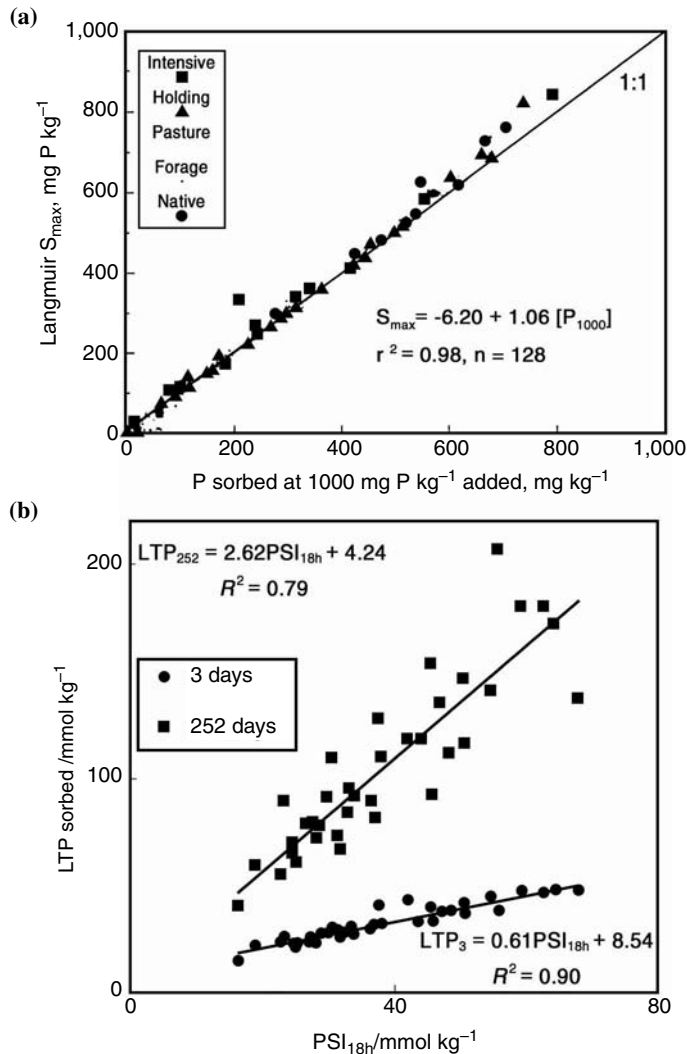


Figure 6.19 (a) Comparison of P sorption maxima calculated by the Langmuir equation using data from eight-point sorption isotherms with a P sorption index (PSI) determined by equilibration of the same soils with a single P solution adding 1000 mg P/kg soil. (From Nair, V. D. et al., *J. Environ. Qual.*, 27, 522–527, 1998. With permission.) (b) Relationships between a PSI determined after 18 h equilibration and P sorbed by 37 Irish soils in 3 and 252 days. (From Maguire, R. O. et al., *Eur. J. Soil Sci.*, 52, 479–487, 2001. With permission.)

Example Problem 6.4

A single-point P sorption isotherm (PSI) is conducted for a soil at a site being considered for a wastewater irrigation system. This is done by adding 10 mL of a 100 mg P/L solution to 1 g of soil, shaking the soil suspension for 24 h, filtering, and analyzing the extract for P. All P removed from solution by the soil is considered to be sorbed. The concentration of P in the filtrate from this soil is 55 mg/L. What is the PSI value for this site? Based on Figure 6.19a, what is the P sorption maxima for each site?

$$PSI \text{ (mg/kg)} = (P \text{ added, mg/kg}) - (P \text{ remaining in solution, mg/kg})$$

$$\text{P added (mg/kg)} = \frac{0.01 \text{ L} \times \frac{100 \text{ mg P}}{\text{L}}}{0.001 \text{ kg soil}} = \frac{1000 \text{ mg P}}{\text{kg soil}}$$

$$\text{P remaining in solution} = \frac{0.01 \text{ L} \times \frac{55 \text{ mg P}}{\text{L}}}{0.001 \text{ kg soil}} = \frac{550 \text{ mg P}}{\text{kg soil}}$$

$$\text{PSI} = \text{P sorbed (mg/kg)} = (1000 \text{ mg P/kg}) - (550 \text{ mg P/kg}) = 450 \text{ mg P/kg soil}$$

Based on Figure 6.19a,

$$S_{\max} = [-6.20 + 1.06 (\text{PSI})] = [-6.20 + 1.06(450)] = [-6.20 + 477]$$

$$S_{\max} = 471 \text{ mg P/kg soil}$$

6.3.3 Mineralization and Immobilization of Soil Phosphorus

Organic P in soils, or P added to soils in organic by-products or crop residues, represents an important source of P for plant growth, as well as a potential source of dissolved and particulate P that may be lost in runoff or leaching. Mineralization refers to the microbially mediated decomposition of organic compounds, resulting in the release of inorganic forms of nutrients into the soil solution. Immobilization, conversely, is defined as the conversion of mineral elements, such as P, by soil microorganisms into biochemical compounds essential for microbial metabolism or into microbial biomass. Mineralization of organic P is largely controlled by the relative amount of C in the organic substrate, which acts as the energy source for the decomposing microorganisms. High C:P ratios provide substantial energy and stimulate microbial growth that consumes all available P; low C:P ratios can result in excess soluble P beyond microbial needs that is then available for plant uptake, leaching, or runoff.

The specific biochemical mechanisms by which organic P is mineralized have been studied for years, but still remain unresolved today. Our current understanding suggests that extracellular phosphatase enzymes produced by plant roots, soil microorganisms, and mycorrhizae are involved in the hydrolysis of organic P to inorganic P. Enzyme production is believed to be related to the amount of bioavailable P in soils, increasing when soils become deficient in P. The nature of organic P and its reactivity with soil constituents also influences mineralization and the availability of organic P for plant uptake and microbial assimilation. Organic P compounds that are strongly sorbed by soils, such as inositol phosphates, may be physically protected from microbial decomposition, at least partially explaining why they are the main form of organic P found in most soils. Other forms of soil organic P, such as orthophosphate diesters, are mineralized rapidly because of their high solubility. Environmental conditions play a key role in the rate and extent of decomposition of organic P. Optimum conditions for mineralization of organic P are similar to those for soil organic N (see Chapter 5). Once mineralized from organic matter, P reverts rather quickly to inorganic forms such as sorbed or precipitated P. In many cases frequent, long-term additions of animal manures and other organic by-products to soils have been shown primarily to increase total inorganic P in soils, not total organic P (Table 6.4).

Organic P can be lost from soils by runoff and leaching and contribute to eutrophication (see Section 6.4). The concentrations of dissolved organic P (DOP) in runoff and drainage waters are usually lower than dissolved forms of inorganic P and are controlled by organic P transformations

in soils, the type of P source applied, soil type, land use, hydrology, and climate. Grassland soils usually have higher DOP values in runoff than arable soils and drainage from peat soils results in greater DOP losses than from mineral soils. Manure additions can provide significant amounts of highly mobile and bioavailable forms of organic P that can be susceptible to transport by runoff and leaching. Soil drying and rewetting strongly influence microbial release of soluble P from organic P compounds. Typically, upon drying and rewetting, there is a flush of release of soluble organic P, most likely due to the rupture of microbial cells caused by rapid rehydration and osmotic shock. Some organic P may also be physically released from coatings on clays and other colloids during soil drying. In general, the mobility of soluble organic P in soils is affected by the reactivity of the particular organic compound with the soil solid phase and the existence of flow processes that can provide pathways for P movement. A conceptual model of organic P transformations in soils shows the complex nature of the interactions between the various types of organic P compounds, the enzymes involved in their degradation, and the major pathways for loss of soluble and particulate organic P to water (Figure 6.20).

6.4 PHOSPHORUS TRANSPORT IN THE ENVIRONMENT

All forms of soil P have been shown to be susceptible to transport from land to water. The fact that the greatest reservoir of P on the Earth is ocean sediments is evidence that “leakage” of P from terrestrial sources to waters is a continuous process. Reducing P transfer to surface waters helps avoid the undesirable effects of eutrophication and the loss of soil productivity as soil P fertility is depleted by erosion. Minimizing P losses is important from a natural resource perspective as well. Most fertilizers are produced by mining and processing geologic deposits of P, a finite resource and energy-intensive industrial process. Similarly, the recycling of organic by-product P as beneficial soil amendments is an important, and usually costly, component of animal agriculture (manures) and municipal recycling programs (biosolids, composts). Practices that prevent soil P loss help to conserve these natural and recycled resources.

The concentrations and loads (mass/area) of P entering a water body are determined by the hydrologic characteristics, land management practices, and point-source discharges in the watershed. Understanding watershed hydrology is critical to reducing P loss because this determines how and where water moves, the flow rates and volumes of moving water, and the extent and time of contact of water with soil and materials on soil surfaces. The terminology used to describe P transfer can be confusing, with many terms lacking clear definitions or having definitions that vary slightly between scientific disciplines. Major terms used to describe the hydrologic pathways of P transfer and spatial and temporal scales appropriate to each term are listed in Table 6.7.

The *key processes* involved in P transfer are those within the soil that affect the *forms* of P present (precipitation–dissolution, sorption–desorption, mineralization–immobilization) and those that refer to mechanisms of P movement, such as *leaching* (eluvation of solutes through soil in percolating water) and *erosion* (physical detachment and movement of soil by wind or water).

6.4.1 Transport of Phosphorus by Surface Flow

Most P is lost from soils by surface processes and pathways (erosion and overland flow) that reflect recent hydrologic events, such as storms, and current land management practices. As shown in Figure 6.21, water flowing across the soil surface can dissolve and transport soluble and easily desorbable P or detach and transport particulate P (Nash et al., 2002). Dissolution refers to chemical processes that solubilize P from soil clays, oxides, or organic matter and is affected by soil P chemistry and the reaction time between flowing water and soils. Detachment refers to physical

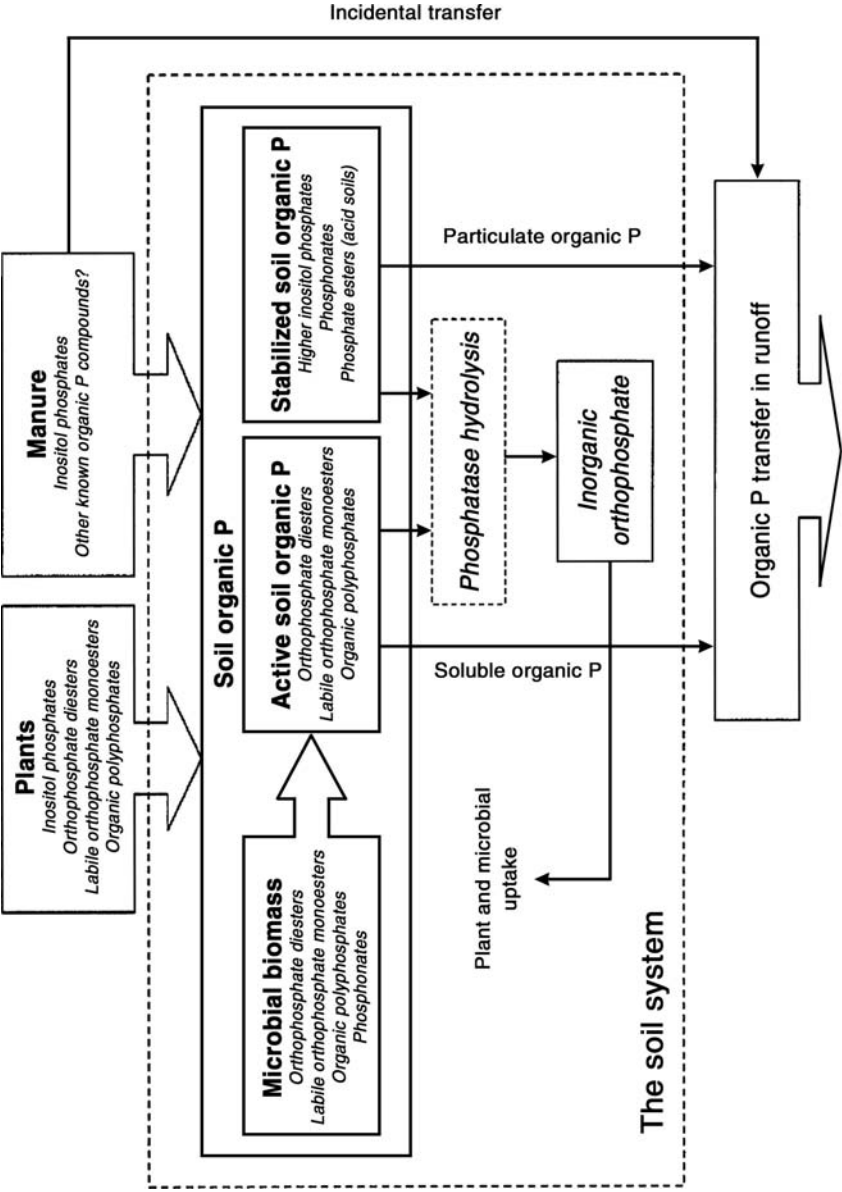


Figure 6.20 Conceptual model of organic P transformations in soils and losses from soil to water. (From Condron, L. M. et al., in *Phosphorus: Agriculture and the Environment*, J. T. Sims and A. N. Sharpley, Eds., ASA-CSSA-SSSA, Madison, WI, 2005. With permission.)

Table 6.7 Suggested Definitions, Preferred Terms (in *italics*), and Classification for Terminology Associated with Hydrochemical Transfer Pathways

Term	Scale	Time	Plane	Definition
Land drainage	Subcatchment	Min/h	Lateral	Water and solute (and entrained solids) export to catchment resulting from land drainage practices: anthropogenic
Runoff	Slope/field	Min/h	Lateral	General hydrological term describing the lateral movement of water off land above- and belowground, causing short-term increases in flow at the catchment outlet
<i>Overland flow</i> , surface runoff	Slope/field	Min/h	Lateral	Movement of water exclusively over the soil surface, down slope, during heavy rain
<i>Interflow</i> , subsurface flow, pipe flow	Slope/field	Min/h	Lateral	Lateral flows below the soil surface; pipe flow refers to lateral subsurface preferential flow
<i>Matrix flow</i> , piston flow, vertical saturated flow	Soil	Days	Vertical	Uniform vertical, downward movement of water, common in very porous soils (e.g., sandy textured)
<i>Preferential flow</i> , bypass flow, macropore flow, vertical unsaturated flow	Soil	Min/h	Vertical	Vertical, downward movement of water through larger subsoil pathways such as root channels, worm holes, cracks, and fissures, often occurring in unsaturated conditions

Note: Classifications are based on the scale, time, and plane at which the terms apply.
Source: Modified from Haygarth and Sharpley, 2000.

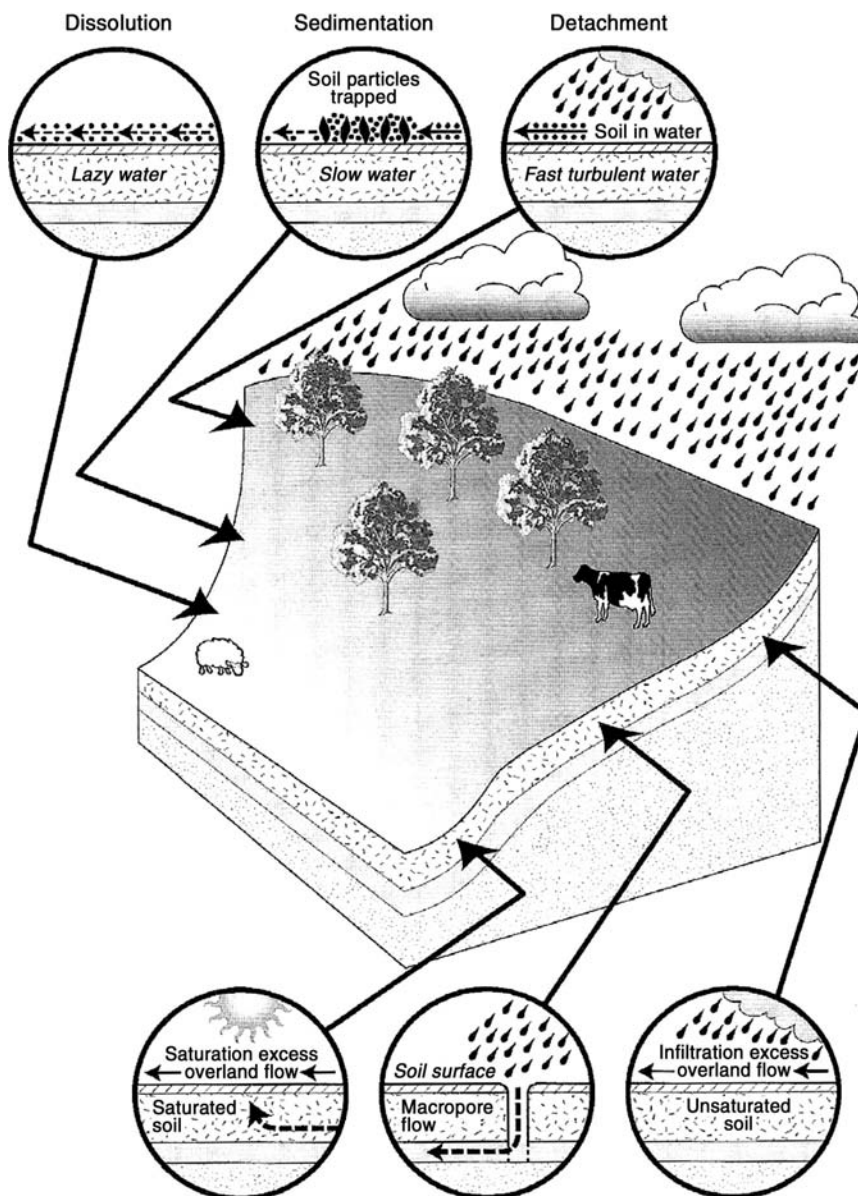


Figure 6.21 Hydrology and pollutant mobilization at the field scale. (From Nash, D. et al., in *Agriculture, Hydrology, and Water Quality*, P. M. Haygarth and S. C. Jarvis, Eds., CAB International, Oxon, U.K., 225–242, 2002. With permission.)

actions that mobilize fine soil particles and particles in soil aggregates by processes such as raindrop impact, the kinetic energy of flowing water, slaking, and dispersion. Soluble P can be either inorganic or organic and particulate P generally consists of finer-sized, lighter soil particles (e.g., silts, clays, fine sands, organic matter). Sedimentation of suspended particles can occur during transport if water flow is slow and physical obstacles to water movement exist (e.g., residues, vegetation in buffer strips). Other important hydrological terms are *infiltration excess overland flow* (infiltration rate of water into the soil profile is limited by poor soil structure or soil compaction, causing water to flow over the surface) and *saturation excess overland flow* (overland flow caused by saturated soil conditions).

In most soils, the quantity of soluble or readily desorbable P susceptible to transport is rather small as a result of the low solubility of P and the considerable sorption capacities of clays and metal oxides for P. This results in most P transport occurring as particulate P. This is particularly true where overland flow contains high quantities of suspended solids, as often occurs during storm flow or snowmelt events. However, if natural or artificial filtration processes exist (e.g., forests, wetlands, grassed waterways, crop residues in reduced tillage systems, grassland pastures) to remove sediment-bound P, then transport of soluble P becomes more important. Similarly, if soils are excessive in P, such as often occurs in areas where organic by-products are frequently applied to cropland, or where long-term no-tillage results in the accumulation of P in the upper few centimeters of soil (see Figure 6.18), the importance of soluble P transfer increases. In these situations, BMPs must not only control soil erosion but also reduce losses of dissolved P.

The mechanisms involved in soluble P transport are straightforward, and include an initial desorption or dissolution of P bound by soil particles, followed by water movement from source soil to a stream, river, or drainage ditch that later discharges into a sensitive water body. Soluble organic P that is not sorbed by soil particles may also be carried by surface or subsurface runoff. Of importance from a soil management point of view is the fact that most of the soluble P in overland flow originates from the interaction of flowing water with the uppermost surface (0 to 2 cm) of the soil. Any management practice that minimizes soluble P concentrations at this depth (e.g., fertilizer or manure incorporation) or enhances infiltration of water into the soil (e.g., artificial drainage), where soluble P can be sorbed by soil constituents, will decrease dissolved P loss. Similarly, nonagricultural areas bordering fields or stream and stream bank sediments can reduce P transport by sorbing P from runoff waters, assuming adequate time of contact between P-enriched waters and soils or sediments.

The transport and subsequent reactions of particulate P are considerably more complex. Particulate P originates not only from soil erosion, but also from the beds and banks of streams or drainage ditches that carry water from a field to a surface water body. As with all erosion, the loss of particulate P represents the detachment of soil particles as a result of the energy contained in falling or flowing water. In some cases wind erosion can also deliver significant amounts of soil to nearby surface waters. The nature of the rainfall or runoff event will determine the energy level of the water, while the texture, structure, and aggregation of the soil will affect the amount of energy required to detach and transport soil particles. As smaller, lighter particles require less energy to dislodge and carry, it is not surprising that clays and organic matter, soil constituents with relatively low particle densities, are preferentially transported in overland flow. Once soil particles enter a watercourse, they eventually settle from the water as sediment. Resuspension of these sediments during intense rainfall events, storms with high winds, or during periods of rapid stream flow can induce particulate P transport at a later date. In general, more intensive land use practices such as urban construction activities, surface mining, and conventionally tilled agricultural soils will result in the highest soil erosion and thus the greatest transport of particulate P. In natural ecosystems and areas where soil conservation practices minimize erosion, the role of stream bank erosion and stream sediments in the transport of particulate P is more important.

The particles transported in runoff are normally higher in P, organic matter, and other nutrients, relative to the soil from which they originated. This enrichment occurs as a result of the greater sorption capacity of finer-sized clay particles and the relatively high concentrations of P in organic matter, relative to silt and sand particles (Table 6.8). The “enrichment ratio” (ER) concept (see Chapter 2) was developed to identify watersheds where more intensive management practices are required to control nutrient loss by erosion. The ER is calculated as the ratio of the concentration of P in the particulate matter found in overland flow to that in the source soil. Research has shown that ERs for total and available P are closely related to the amount of soil lost from a watershed. This provides a quantitative basis for estimating the watershed-scale impact of land use on P loss,

Table 6.8 Average Enrichment Ratios for Six Western Soils

Soil Property	Enrichment Ratio ^a
Organic Carbon	2.00
Clay (%)	1.56
Surface Area	1.32
Bioavailable P	1.49
Total P	1.46
EPC ₀ (mg/L)	-1.80 ^b

^a Enrichment ratio = $\frac{[\text{Value of soil property in runoff sediment}]}{[\text{Value for soil property in source soil before runoff}]}$

^b EPC₀ = equilibrium P concentration at zero sorption. Negative enrichment ratio indicates that source soil maintained a higher P value in solution at equilibrium than runoff sediment.

Source: Adapted from Sharpley, 1985.

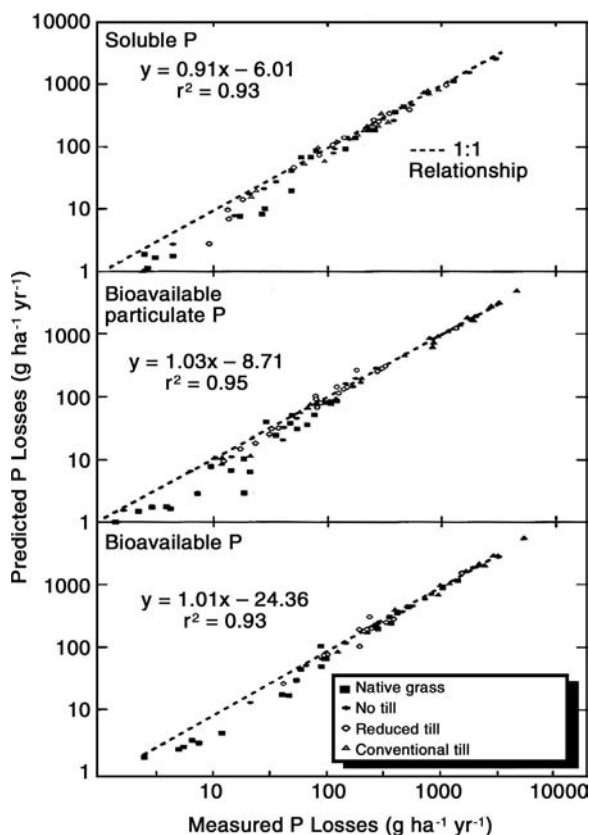


Figure 6.22 Comparison of predicted and measured losses of P. Soluble P was predicted from soil loss, soil test P, and variables related to runoff. Bioavailable P was predicted from soil total or bioavailable P, sediment concentration in runoff, and enrichment ratios estimated from soil loss. (Adapted from Sharpley, A. N. and A. D. Halvorson, in *Soil Processes and Water Quality*, R. Lal, Ed., Advances in Soil Science, Lewis Publishers, Boca Raton, FL, 1994.)

soil productivity, and water quality. Recently, computer models have been reasonably successful in predicting P loss from readily obtainable parameters such as soil erosion, soil test P, and soil properties associated with the range of values for soil series found in the landscape (e.g., ER, clay content, organic matter, total P) (Figure 6.22).

Virtually all dissolved P transported via overland flow is biologically available, but particulate P that enters streams and other surface waters must first undergo a solubilization reaction (e.g., desorption, change in oxidation–reduction conditions, mineralization) before becoming available for aquatic biota. Complicating the matter further is that, during the transport process itself, soluble and particulate P can undergo reactions with soils bordering fields and lakes, with suspended sediments in flowing waters, and with streambed and stream bank sediments. For example, dissolved P can be resorbed by suspended sediments in overland flow and in stream channels. These reactions can dramatically alter the potential for the P originally lost from a soil by overland flow to induce eutrophication downstream.

Once particulate P has entered a lake, many of the processes operating in the soil P cycle continue, albeit at different rates. The size of the particles along with the relative temperatures of the inflowing water and the lake influence the initial distribution of the sediments within the lake. One of the major causes of eutrophication is the high degree of turbidity associated with fine-sized particles that settle very slowly to the lake bottom. The turbid nature of the upper water column reduces light penetration, decreasing the photic zone. As the finer-sized particles are usually higher in P than the quickly settling coarser particles, the overall initial effect is to stimulate biological productivity in the epilimnion (upper layer of the water column). Of long-term importance, however, is the later desorption or dissolution of P from sediments that, with time, have settled to lake bottom. The P sorbed by clays, Fe and Al oxides, and CaCO_3 are the main sources of potentially desorbable P in benthic sediments.

The physical and chemical processes operational in surface waters greatly influence the desorption or dissolution of P from sediments. Changes in temperature, or turbulence induced by storms, can resuspend bottom sediments in the water column and enhance the desorption of P in photic zones where algal growth occurs. The O_2 status of the water body can also affect desorption or dissolution of P from sediments. Studies have shown, for example, that under anaerobic conditions P release from lake sediments was enhanced, usually due to reductive dissolution of Fe-P minerals or ferric (Fe^{3+}) oxides containing sorbed P. Similar results were obtained with sediments from agricultural ditch drainage systems where Fe-P compounds were shown to dissolve under reducing conditions and release P into solution (Figure 6.23). However, it is also known that when lake O_2 levels increase, P sorption capacity can be restored and dissolved P concentrations decreased due to the reprecipitation, at the sediment–water interface, of amorphous ferrous hydroxide ($\text{Fe}(\text{OH})_2$) like solid phases with high surface areas. Therefore, the potential for P release from sediments (or flooded soils) will be strongly influenced by the redox status at this interface. Reducing conditions in sediments can cause release of P and Fe into sediment porewaters. However, if oxidizing conditions exist at the interface, as dissolved P and Fe diffuse into the overlying water, reprecipitation of Fe dissolved from soils and simultaneous sorption of dissolved P can occur and mitigate movement of P from reduced soils or sediments to overlying surface waters. This is shown in Figure 6.23c, which depicts temporal changes in dissolved Fe and P in a soil flooded for 60 days. Dissolved P and Fe^{2+} increased in porewaters with time, but floodwater P decreased because the overlying floodwaters remained oxidized throughout the study. Thus, P was released from porewaters of the reduced, flooded soil, but did not enter the overlying water because it was resorbed at the oxidized interface.

The mean residence time of water in a lake also greatly affects the importance of sediment P in eutrophication. When inflowing water has a long mean residence time (at least several months), P inputs from streams and rivers have sufficient time to accumulate as sediments on lake bottoms. If water flow through the lake is rapid, however, P retained by finer-sized particles may be removed from the lake prior to settling from the water column. Indeed, one common strategy used in urban

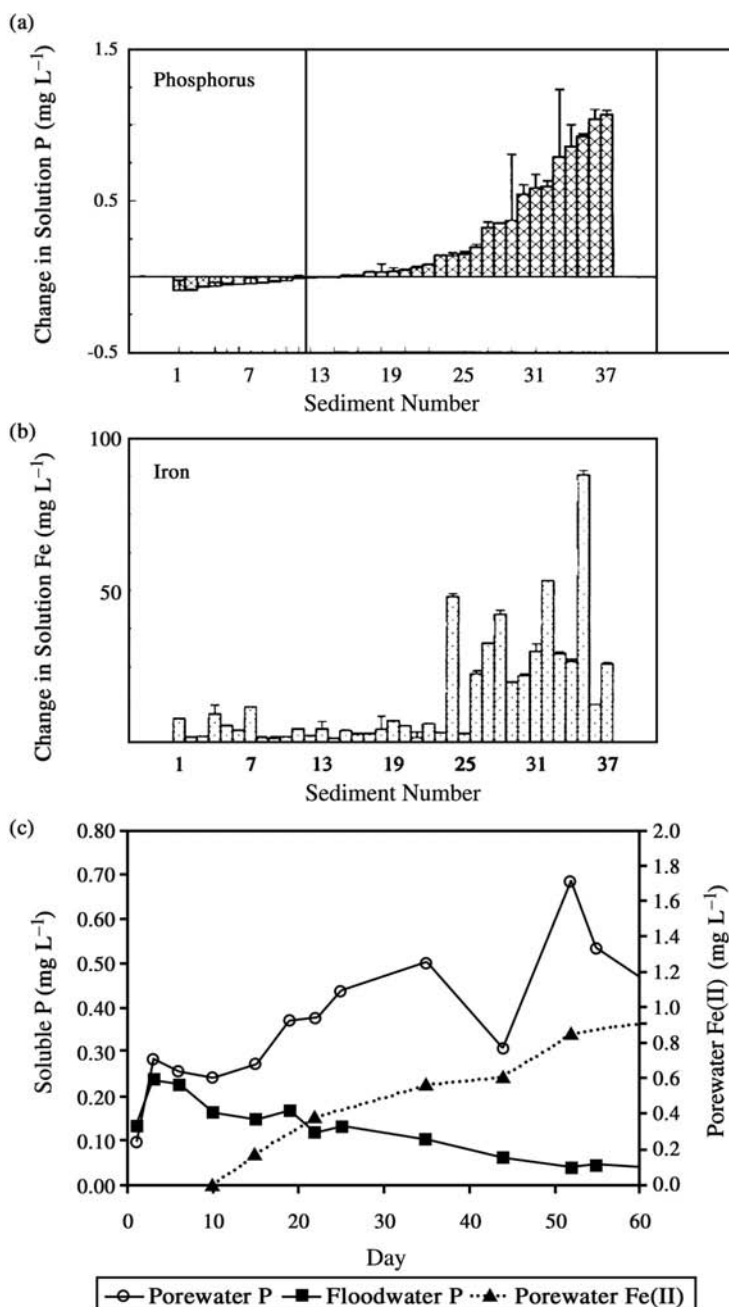


Figure 6.23 Effect of reducing conditions on (a) P and (b) Fe (II) solubility in 37 sediments from agricultural drainage ways. Vertical bars are the change in Fe or P concentration following incubation of sediments under anoxic conditions. The concurrent release of P and Fe from sediments under reducing conditions indicates that Fe-P compounds in sediments may be a source of P to overlying waters under anoxic conditions. (From Sallade, Y. E. and J. T. Sims, *J. Environ. Qual.*, 26, 1579–1588, 1997. With permission.) (c) Temporal changes in porewater and floodwater P and porewater Fe (II) in a flooded soil. (From Young, E. O. and D. S. Ross, *J. Environ. Qual.*, 30, 91–101, 2001. With permission.)

and agricultural situations to minimize nutrient enrichment of lakes and reservoirs is to install settling ponds, impoundments, or constructed wetlands with long residence times to act as filtration

systems for particulate P in overland flow. Subsequent removal or chemical “sealing” of the enriched sediments by adding materials such as alum (aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$) may still be needed, but can be anticipated and planned for maximum efficiency.

6.4.2 Phosphorus Leaching and Subsurface Flow

Leaching and subsurface lateral flow of P (interflow) are normally less of a concern for P transfer because of the potential for P retention in the soil profile. Exceptions are soils with high degrees of P saturation, soils with preferential flow, and soils subjected to artificial drainage (tiles, ditches). Soils that are saturated with P have reduced capacities to retain P and can maintain soluble P concentrations high enough to be of concern for loss by matrix flow (uniform, vertical, downward movement of water) or preferential flow. Preferential flow is the rapid leaching of water and solutes through natural channels, fissures, and structural voids in the soil in a manner that bypasses most of the soil matrix. As shown in Figure 6.24, flow of this sort can rapidly transport P from surface soils to tile lines and shallow water tables. Preferential flow is greater in soils with higher “cracking potential” (soils that swell and shrink as soils wet and dry due to a high amount of 2:1 expanding clay minerals) or soils with well-established root channels (e.g., pastures, forages, long-term no-tilled cropland). Artificial drainage systems “short-circuit” the movement of water, dissolved solutes, and even fine soil particles that would normally leach slowly through the soil to groundwaters and eventually discharge, through base flow, to surface waters. Tiles and drainage ditches, by design, result in a much more rapid discharge of percolating waters and shallow groundwaters to surface waters. However, they also reduce losses of P in overland flow by increasing infiltration of water into the soil. In general, any hydrologic pathway that reduces the contact time between water and the soil matrix is of some environmental concern because it decreases the likelihood that P will be retained via sorption and precipitation reactions.

The natural process of groundwater discharge into surface waters contributes P that can play a role in eutrophication. In most instances the input of P by subsurface flow represents the effect of decades of land use and must be viewed as a baseline contribution that can only be altered by long-term improvements in management of all urban and agricultural operations in a watershed (see Table 6.2). One possible exception is the subsurface discharge from artificially drained fields, where

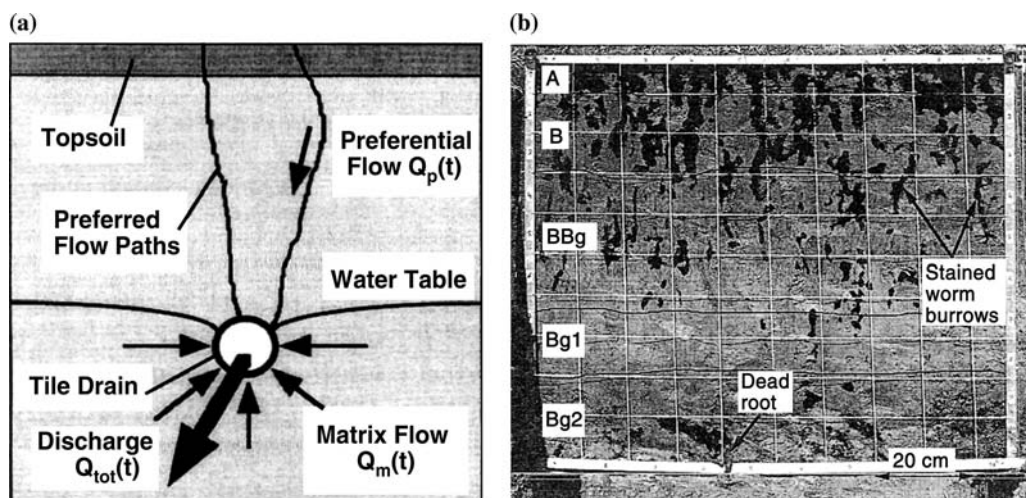


Figure 6.24 (a) Conceptual model showing the two components of tile drainage, matrix flow and preferential flow; (b) use of dye tracers to characterize preferential flow paths in the soil profile. (From Stamm, C. et al., *J. Environ. Qual.*, 27, 515–522, 1998. With permission.)

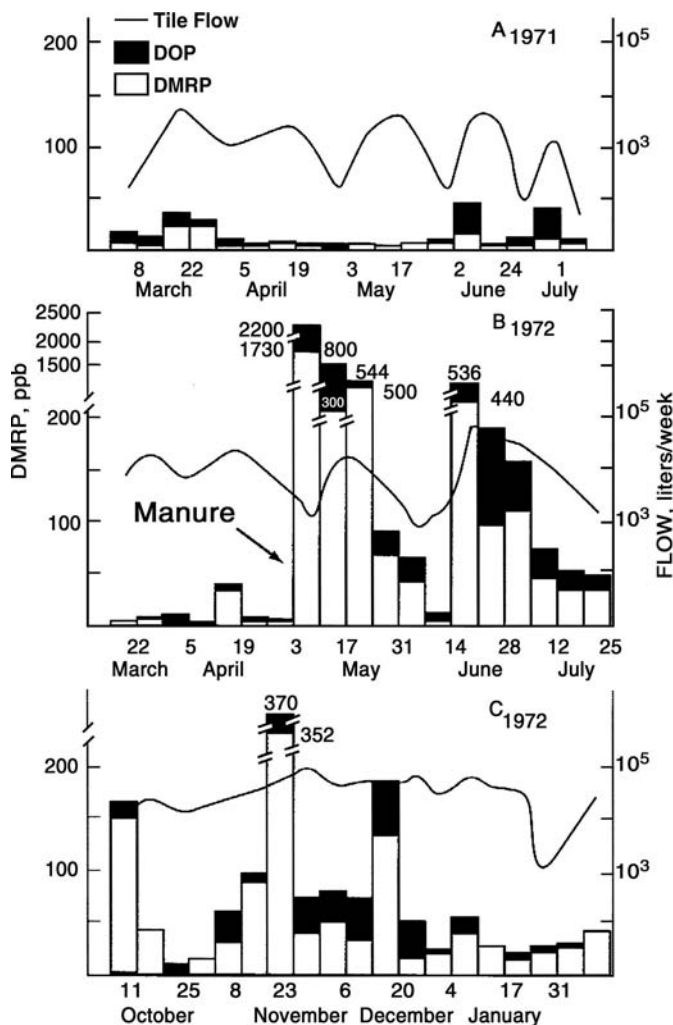


Figure 6.25 Effect of dairy manure application (200 Mg/ha) and tile flow on the loss of dissolved organic P (DOP) or dissolved inorganic P (DMRP = dissolved molybdate reactive P) in tile drainage during a 2-year period. (From Hergert, G. W. et al., *J. Environ. Qual.*, 10, 338–344, 1981. With permission.)

corrective measures can be taken at either the source or at the point of discharge. Improved nutrient management programs and artificial wetlands are examples of strategies that can be used to reduce nutrient loads in drainage waters from urban and agricultural areas.

In most cases the concentrations of P in subsurface flow have been found to be quite low and well below any eutrophication thresholds. This reflects the considerable P sorption capacity of soils, particularly in P-deficient subsoil horizons. Because of this, P leaching, unlike NO_3^- leaching, is rarely viewed as an important environmental issue. Exceptions include organic soils with fluctuating water tables, soils where preferential flow is significant, and heavily manured, sandy soils with shallow water tables. The role of organic matter in P leaching, mentioned above, is not well understood, but is believed to be important. Artificial drainage, commonly used in organic and poorly drained soils, normally increases infiltration and percolation of water, increasing the likelihood of P leaching, but decreasing P losses in runoff. If heavy applications of animal manure are combined with artificial drainage of soils, P leaching and loss via subsurface pathways can be

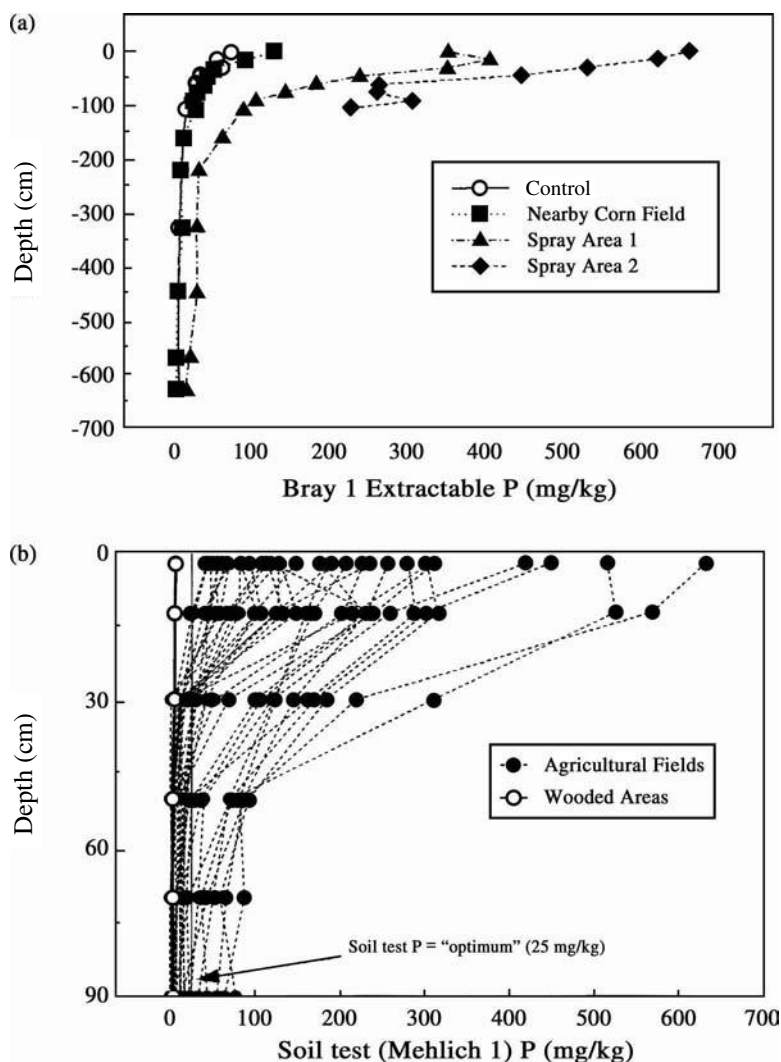


Figure 6.26 Phosphorus leaching studies illustrating distribution of soil test P with depth; soil tests: Bray P ($0.03 \text{ M NH}_4\text{F} + 0.025 \text{ M HCl}$); M1-P (Mehlich 1, $0.05 \text{ M HCl} + 0.0125 \text{ M H}_2\text{SO}_4$). (a) A wastewater irrigation system compared with a commercially fertilized corn field. (Adapted from Adriano et al., 1976.) (b) 34 agricultural soils from Delaware where animal manures are regularly applied. (Adapted from Mozaffari and Sims, 1994.)

significant, as shown in Figure 6.25 where the application of 200 Mg/ha of dairy manure sharply increased dissolved P concentrations in tile drainage. Improved aeration in organic soils due to artificial drainage has also been shown to stimulate P mineralization and loss in drainage waters via leaching and shallow groundwater discharge.

The most common situations where P leaching from mineral soils has been observed are in municipal and agricultural wastewater treatment systems and sandy soils where manure use regularly overapplies P to soils because of the lack of suitable land for proper manure management. Examples are shown in Figure 6.26 for sandy soils used for a wastewater irrigation system and agricultural cropland in an area dominated by a highly concentrated poultry industry. In the case of the wastewater irrigation system, groundwater P values in the areas irrigated with wastewaters averaged 0.75 mg/L, relative to a local environmental standard of 0.05 mg/L.

Environmental Quality Issues/Events

Developing and Implementing the Phosphorus Site Index: A National Research and Extension Project in the United States

Although the importance of integrating soil P cycling and transport into a holistic approach to prevent nonpoint-P pollution of surface waters is widely accepted, significant obstacles often arise to the implementation of improved P management practices. Foremost is the availability of human and economic resources needed to design and implement new programs that are usually more intensive and expensive. When resources are limited, prioritizing the areas in a watershed in terms of their relative potential for P loss to water is critical. This requires the efforts of multidisciplinary teams with expertise in aquatic ecology, hydrology, soil science, crop production, urban and industrial by-product management, engineering, and natural resource economics. Once the priorities are established, available resources can be directed toward improving P management and reducing P impacts on water quality.

Computer-based, water-quality models have been developed to guide P management at larger scales and over longer time periods. Examples include EPIC (Erosion-Productivity-Impact-Calculator), FHANTM (Field Hydrology and Nutrient Transport Model), and GLEAMS (Ground Water Loading Effects on Agricultural Management Systems). These models have been shown to predict changes in soil P concentrations, crop yield responses, and P losses to water with reasonable accuracy. However, they are limited by the need for large databases, with many parameters that can be difficult to obtain and keep current, such as site-specific soil properties and processes, site hydrology, crop rotation and management, and climate.

Simpler approaches that can be used by advisory agencies (Cooperative Extension, USDA Natural Resources Conservation Service, NRCS) or nutrient management consultants are also available. One example is the P site index system adopted by NRCS as a component of its Code 590 national conservation practice nutrient management standard (see <http://www.nrcs.usda.gov/technical/ecs/nutrient/590.html> for details). The P site index was developed by a national committee of soil scientists from U.S. universities and government agencies in the early 1990s. From the outset, the goal was to develop an approach to predict the potential environmental impact of soil P using easily accessible, site-specific information. As originally proposed, the P site index integrated agronomic soil test P data with other site characteristics that quantified soil erosion and overland flow, and P fertilizer and/or organic P source application rate, method, and timing in a simple, weighted matrix system (Lemunyon and Gilbert, 1993). Each characteristic was assigned an interpretive rating with a corresponding numerical value, Low (1), Medium (2), High (4), or Very High (8), based on the relationship between the characteristic and the potential for P loss from a site. Suggested ranges appropriate to each rating for a site characteristic were then assigned. Each of the characteristics in the P index was also given a weighting factor that reflects its relative importance to P loss. Weighting factors were based on the professional judgment of the scientists that developed the P index. For example, erosion (weighting factor = 1.5) was considered more important to P loss than P fertilizer application method (weighting factor = 0.5). The intent of those developing the P site index was that each state or region would modify the ratings, values, and weighting factors in a manner appropriate to local conditions as more research data became available on soil properties, hydrology, climate, and P management practices. This has occurred and many variations of the original P site index are in place today, such as the P Site Index for Delaware and Maryland shown in Figure 6.27 (see <http://pswmru.arsup.psu.edu/phosphorus/nprpresources.htm> for examples of other P site indices for the United States). Examples of modifications to the P site index that have been included, or considered, are: adding catchment factors (condition of receiving water, and ratio of land:water) that reflect the sensitivity of the affected water body to P inputs, the proximity of a field to receiving waters; converting the P site index from its original additive form to one that assesses P transport and P source management separately and then multiplies them together, as was done in Delaware and Maryland. This avoids the situation where a very high soil test P value in an area with little or no overland flow or erosion results in a very high P site index value; similarly, it allows for sites with low soil test P values and high erosion potentials or poor P management to be identified as high-risk areas in need of more intensive BMPs. Other factors such as soil drainage class, soil texture and cracking potential, and information on high water tables and/or depth of tile drain lines may be needed in regions where P leaching and subsurface lateral flow to streams and

Part A: Phosphorus loss potential due to site and transport characteristics.

Characteristics	Phosphorus Loss Rating					Value
Soil Erosion	2 x [Soil erosion value from RUSLE (tons/acre)]					
Soil Surface Runoff Class	Very Low 0	Low 2	Medium 4	High 6	Very High 8	
Subsurface Drainage	Very Low 0	Low 2	Medium 4	High 6	Very High 8	
Leaching Potential	Low 0		Medium 2	High 4		
Distance from Field to Surface Water	> 100 ft 0	< 100 ft AND > 50 ft vegetated buffer OR < 100 ft AND > 25 ft vegetated buffer AND > 25 ft additional no P application zone 2	< 100 ft AND > 25 ft vegetated buffer AND < 25 ft additional no P application zone 4	< 100 ft AND < 25 ft vegetated buffer AND > 25 ft additional no P application zone 6	< 100 ft AND < 25 ft vegetated buffer AND < 25 ft additional no P application zone 8	
Priority of Receiving Water	Very Low 0	Low 1	Medium 2	High 3	Very High 4	

Sum of Site and Transport Characteristics: _____

Scaling factor: $\times 0.02$

Total Site and Transport Value for Part A: _____

Part B: Phosphorus loss potential due to P source and management practices.

Characteristics	Phosphorus Loss Rating					Value
Soil Test P Fertility Index Value (FIV)	[0.2] x [FIV from University of Delaware Soil Test]					
P Fertilizer Application Rate	[0.6] x (lbs P ₂ O ₅ applied per acre)					
P Fertilizer Application Method and Timing	None applied 0	Injected/Banded below surface at least 2" 15	Incorporated within 5 days of application 30	Surface applied March through November OR incorporated in > 5 days 45	Surface applied December through February 60	
Organic P Source Application Rate	[Phosphorus Availability Coefficient (PAC; default=0.6)] x (lbs P ₂ O ₅ applied per acre)					
Organic P Source Application Method and Timing	None applied 0	Injected/Banded below surface at least 2" 15	Incorporated within 5 days of application 30	Surface applied March through November OR incorporated in > 5 days 45	Surface applied December through February 60	

Total P Source and Management Value for Part B: _____

P Site Index	Generalized Interpretation of P Site Index
< 50	LOW potential for P movement from this site given current management practices and site characteristics. There is a low probability of an adverse impact to surface waters from P losses from this site. Nitrogen-based nutrient management planning is satisfactory for this site. Soil P levels and P loss potential may increase in the future due to N-based nutrient management.
51 - 75	MEDIUM potential for P movement from this site given current management practices and site characteristics. Practices should be implemented to reduce P losses by surface runoff, subsurface flow, and erosion. Nitrogen-based nutrient management should be implemented no more than one year out of three. Phosphorus-based nutrient management should be implemented two years out of three during which time P applications should be limited to the amount expected to be removed from the field by crop harvest or soil test P based application recommendations, whichever is greater.
76 - 100	HIGH potential for P movement from this site given current management practices and site characteristics. Phosphorus-based nutrient management should be used for this site. Phosphorus applications should be limited to the amount expected to be removed from the field by crop harvest or soil test P based application recommendations. All practical management practices for reducing P losses by surface runoff, subsurface flow, or erosion should be implemented.
> 100	VERY HIGH potential for P movement from this site given current management practices and site characteristics. No phosphorus should be applied to this site. Active remediation techniques should be implemented in an effort to reduce the P loss potential of this site.

Figure 6.27 Phosphorus P site index system used in Delaware and Maryland to rate sites for their potential to deliver P to sensitive water bodies. (Adapted from Coale et al., 2002; Leytem et al., 2003.)

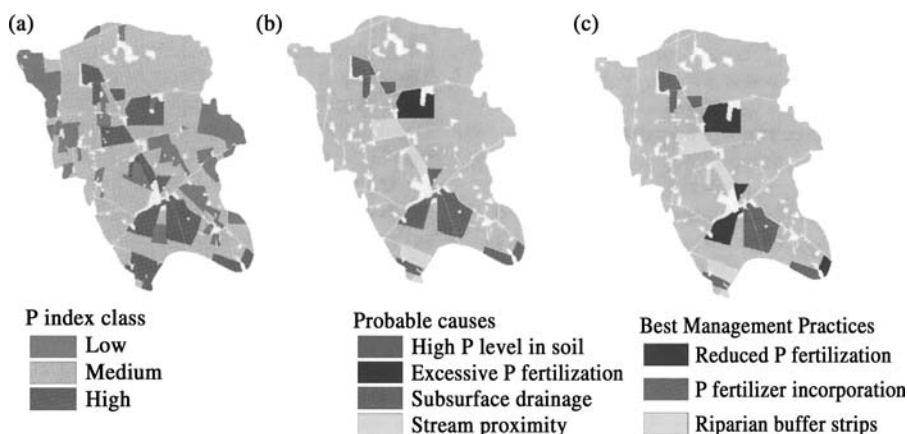


Figure 6.28 Application of the P site index approach to the Vemmenhog watershed in Sweden. (a) P site index classes determined using the Maryland P site index. (From Coale et al., 2002.) (b) Probable causes of high P site index values; (c) suggested BMPs to control P loss. (From Djodjic, F. et al., *J. Environ. Qual.*, 31, 937–946, 2002. With permission.)

drainage ditches are important paths for P transport. Data from routine or special soil tests, such as pH, organic C, extractable Al, Fe, Ca, and Mg, and tests for water soluble P or the degree of soil P saturation may also be useful in identification of soils with higher potentials for P loss. It has also been suggested that a P source coefficient be used to account for the differences in P solubility and bioavailability known to exist between different types of fertilizers, manures, and biosolids.

Although developed in the United States, the P site index approach is now being evaluated worldwide. For example, an application of using the P site index approach to guide identification of areas of high P loss, likely causes of P loss, and the best BMPs to reduce P loss in a Swedish watershed is shown in Figure 6.28.

PROBLEMS

- 6.1 Visit the Chesapeake Bay Program Web site and review the section on “Nutrient Pollution” (<http://www.chesapeakebay.net/index.cfm>). What are (a) major sources of phosphorus pollution of the bay; (b) the reduction in P loading needed to restore the health of the bay; (c) key strategies identified to achieve these reductions?
- 6.2 Soils contain large quantities of total P, often much more than is needed for economically optimum crop yields. Assume the total P concentration of the topsoil (0 to 15 cm depth) in a field used for silage corn production is 1000 mg/kg. The total P concentration in corn silage is 0.06%. Calculate the total amount of P in the topsoil (assume that the topsoil has 2.24×10^6 kg soil/ha) and the total amount of P removed in harvested silage (assume a silage yield of 70 Mg/ha). Express your results in kg P/ha. Explain why it might be necessary to add fertilizer or manure P to this soil to achieve optimum silage yields.
- 6.3 In a mine spoil reclamation project you have the option of using rock phosphate, triple superphosphate, or composted biosolids to build soil P fertility to an “optimum” level for the conservation grasses and trees to be grown. If the amount of P recommended to raise the soil from a “very low” to “optimum” value was 90 kg P/ha, how much of each material, in pounds per acre, would you need to apply, based on the P composition values of these materials (given in Table 6.5)? Assume you decided to use composted biosolids because it was the most cost-effective source. What other crop production and environmental factors would you need to consider before applying compost to the mine spoil?

- 6.4 Explain the difference between the following soil processes that are relevant to both plant availability and environmental impacts of soil P: (a) desorption and dissolution; (b) erosion, runoff, and leaching.
- 6.5 Sorption isotherms are useful for comparing P sorption capacities of soils with differing physical and chemical properties or management histories. You are provided the following data from sorption isotherm experiments with two soils:

Initial P Concentration (P_{eq} , mg P/L)	Final P Concentration at Equilibrium (P_{eq} , mg P/L)	
	Soil 1	Soil 2
0	0.5	0.02
1	0.8	0.05
2	1.2	0.10
4	2.6	0.2
10	7.75	1.2
20	17.7	5.2
40	37.1	22.0

- Calculate the amount of P sorbed (P_{sorb}) for both soils. Then plot (a) P_{sorb} vs. P_{eq} for each soil (sorption isotherm) and (b) the linearized version of the Langmuir equation (Equation 3.8). Using the linearized version of the Langmuir isotherm, calculate k and b . Contrast the suitability of the two soils for (a) use in a wastewater irrigation system where disposal of high P wastewaters is desired; and (b) growth of alfalfa, a crop with a high P requirement (assume both soils have a low soil test P value).
- 6.6 Soluble and bioavailable P in soils is commonly measured by rapid soil extraction (shaking the soil and a chemical solution at a specific soil:solution ratio for a defined time, followed by filtration) and colorimetric analysis of the P concentration in the extracted solution. A key aspect of all colorimetric procedures is the use of a standard curve that relates known concentrations of the element of interest to the absorbance of light by the colored solution that results when the element reacts with added chemical reagents. In the case of P the chemical reagents that are added (e.g., ammonium molybdate) react with orthophosphate, forming a blue color that increases in intensity in proportion to the concentration of P in solution. This technique is commonly referred to as the “Murphy–Riley” method. Assume you are asked to determine the amount of water-soluble and plant-available P (as determined by the Mehlich 1 soil test) in soil from a cornfield near a surface water sensitive to eutrophication where there is concern about overfertilization of soils with P and losses of P in runoff. You extract the soil with deionized water (soil:solution ratio = 1:10) and the Mehlich 1 soil test (soil:solution ratio = 1:4). You then prepare a series of P standards and measure the absorbance of light by each standard solution and by the two samples and obtain the following results:

Standard Curve and Sample Absorbance Results	
P Concentration (mg/L)	Absorbance
Standard Curve	
0.2	0.12
0.4	0.24
0.6	0.35
0.8	0.47
1.0	0.62
Soil Sample:	
	Water soluble: 0.13
	Mehlich 1: 0.88

- a. Plot the standard curve and calculate the amount of water-soluble and plant-available P in the soil in mg P/kg, in lb P/acre, in lb P_2O_5 /acre, and in kg P/ha.

- b. If the “optimum” soil test P value for corn production is 25 mg P/kg (Mehlich 1 soil test), would you recommend that P be applied to this field?
- 6.7 Some more complex soil testing procedures can be used to “fractionate” the total P in soils into Al-P, Fe-P, and Ca-P. This is done by sequentially extracting the same soil sample with stronger or more selective chemical reagents. Assume you conduct a fractionation procedure for soil P and obtain the following results:

Form of Soil P	Extracting Solution	Soil:Solution Ratio	P Concentration in Solution (mg/L)
Aluminum-P	0.1 <i>N</i> NaOH	1 g and 40 mL	21.4
Iron-P	0.5 <i>M</i> citrate-dithionite bicarbonate	1 g and 25 mL	23.7
Calcium-P	1 <i>N</i> HCl	1 g and 50 mL	3.2

- a. Calculate the amount of P in each fraction in mg/kg.
- b. Calculate the percent of P in each fraction, using the “sum of fractions” to represent total P.
- 6.8 One approach to restoring eutrophic lakes has been to add alum (aluminum sulfate) directly to the lake. Upon dissolution, the alum interacts with lake-bottom sediments and prevents P release into overlying waters. Explain the mechanism by which alum prevents P release from sediments. Would iron sulfates be a suitable alternative material to alum?
- 6.9 Explain why soil conservation and nutrient management practices for P have traditionally focused on reducing P losses by soil erosion, while those for N have been directed toward reducing nitrate leaching.
- 6.10 Assume you are working as a consultant in an area dominated by soils that contain 2:1 clays and thus have a high “shrink–swell” potential (“cracking soils”). The soils also contain tile drains that discharge into nearby surface waters and P leaching from manure applications has been identified as a serious water quality problem. What BMPs could be used to reduce P losses by leaching in this setting?

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7.1 INTRODUCTION

Sulfur (S) exists in the atmosphere, hydrosphere, biosphere, and lithosphere as various chemical species with a wide range of oxidation states. Environmental impacts are primarily the result of atmospheric pollution and acidic deposition from gaseous S emissions (see Chapter 11), as well as acid soils, *acid mine drainage* (AMD), and groundwater contamination from aqueous S species. Both biological and physicochemical processes are the driving forces in the sulfur cycle. Because S is a secondary macronutrient, along with calcium (Ca) and magnesium (Mg), and is required for plant, animal, and human subsistence, both toxicities and deficiencies can occur depending on geomorphology, soil conditions, cultural practices, water regimes, and climatic influences. To manage S properly, we must understand its role in the environment. First, we know, with respect to our concern with S in the environment, that acidic deposition and acid-producing soils and subsurface materials are the most formidable problems that must be addressed. Second, S is an essential plant nutrient that has received greater attention recently because of the reduction in S-containing materials (e.g., low-S fertilizers, use of non-S pesticides, and reduced atmospheric S deposition) added to croplands, pastures, and forest ecosystems. These reductions increase the probability of S deficiencies in certain crops and tree species. Third, it is essential that we appreciate the connection among S and the other biogeochemical cycles, including the essential elements — carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P) — and micronutrients. This chapter discusses the role of S in agricultural, forest, mine land, salt-affected, and aquatic ecosystems, with special emphasis on environmental concerns, biogeochemistry, inorganic and organic forms, retention, transformations, nutrition, and management.

7.2 IMPORTANCE OF SULFUR

Sulfur is an *essential nutrient* that is required for all biological organisms including plants, animals, microorganisms, and humans. Although both S deficiencies and toxicities have been extensively reported for plants and animals, cases involving plant S deficiencies are more significant because S-deficient areas have been reported throughout the world. Sulfate (SO_4^{2-}), the predominant soluble form of soil S taken up (e.g., absorbed) by plants, however, is not the form that comprises the majority of S found in soils, which includes organic S and S minerals. This explains, at least partially, why certain areas may exhibit plant S deficiencies despite what may seem to be adequate soil S concentrations. Low S parent materials, high rainfall, intense leaching, and extremely weathered soils, along with low S atmospheric deposition, are common conditions in S-deficient areas.

Sulfur occurs naturally in several inorganic and organic forms that are part of the biogeochemistry of the global S cycle and is an integral component of C, N, and P cycles (David et al., 1995; Guggenberger and Haider, 2002). The major S pools are found in the lithosphere, similar to P, with rock minerals containing S concentrations ranging from 0.026 to 10% or more. However, the global S cycle functions much like that of N, with the lithosphere comprising major N and S pools. Although most of the S that cycles through the atmosphere is a result of human activity, the atmospheric S pool is relatively small in comparison with other S pools. The short *mean residence time* (MRT) of atmospheric S compounds actually results in more S cycling through the atmosphere than N (i.e., S flux is greater than N flux). Soil S transformations are predominately controlled by microbially mediated processes, which also play an important role in the availability of S to plants.

7.2.1 Sulfur Nutrition

Like N, S is an essential element in several *amino acids* (cysteine, cystine, and methionine) that are part of plant, animal, microbial, and human proteins; S is also an important constituent in *vitamins*

and *hormones*. Sulfur plays an active role in plant structural composition and metabolic processes, and is also crucial to animals because S performs several functions in structural, metabolic, and regulator processes. Sulfur has often been overlooked as an essential plant nutrient primarily because, until recently, S deficiencies were not very common. The importance of S in plant nutrition and the determination of S availability are discussed further in Sections 7.5.1 and 7.5.2.

For animals, S-containing amino acids are integral components of many *biochemical constituents* including proteins, enzymes, and some hormones. Organic S-containing biochemical compounds are important to the production of animal bones, tendons, cartilage, skin, and heart valves. The major structural protein in animals is collagen, which contains S amino acids. Enzymatic S plays an essential role in enzyme activity and function. Sulfur deficiencies in animals may be manifested as decreased or slow weight gains, lethargy, reduced milk, egg, or wool production, as well as several other symptoms, and if S deficiency is prolonged, possibly death. In addition, the form of S supplied to animals is critical because nonruminants are unable to utilize inorganic S compounds. Ruminants, such as sheep and cattle, are capable of metabolizing inorganic forms of S through the activity of rumen microorganisms. A constant supply of S is required for proper growth in plants and animals, and is critical for animals because S is not stored in their bodies.

Sulfur toxicity is also a potential problem for plants and animals. For plants, S toxicity may be exhibited through retarded growth, interveinal chlorosis that extends along leaf margins, or premature senescence of leaves. However, except for citrus, most crops appear to be unaffected by high SO_4^{2-} levels, and for those plants that do display symptoms, it is generally the associated cation that is detrimental. The toxic effect of gaseous sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) compounds on plants is discussed further in Section 7.5. As for animals, S toxicity is primarily a function of the S species. Ruminants have suffered from S toxicity when ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ or gypsum (CaSO_4) were used as nonprotein N or Ca supplements, respectively. Nonruminants suffer from S toxicity when they consume excessive amounts of S-containing amino acids, especially methionine, in their diet.

7.2.2 Environmental Impacts of Sulfur

Environmental concerns related to S are listed in Table 7.1. *Acidic deposition* results from the oxidation of S and N in the atmosphere and is discussed in greater detail in Chapter 11. *Acid soils* and *AMD* occur when reduced S compounds and minerals are oxidized to form sulfuric acid (H_2SO_4). Examples of AMD are most prevalent at inactive or abandoned mine sites, which continue to be of greatest environmental concern and liability for the mining industries. In the United States, AMD and other toxins from abandoned sites have polluted in excess of 75,000 ha of impoundments and lakes as well as more than 20,000 km of streams and rivers. The U.S. Bureau of Mines has estimated the cost of remediating the affected waterways at \$30 to \$75 billion.

A *drinking water standard* of 250 mg SO_4/L was established because SO_4^{2-} has been found to act as a laxative in some humans and animals. In addition, *geothermal activity* can influence the surrounding soil and plant ecosystems by releasing significant amounts of gaseous S into the atmosphere. Sulfate is highly soluble and is known to accumulate in soils and groundwaters of arid and semiarid environments.

Burning of fossil fuels, industrial processes — petroleum refining and processing of metals such as copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) — and other activities (biofuel and biomass emissions, and agriculture) have resulted in enormous amounts of S emitted into the atmosphere every year (Table 7.2). Atmospheric forms of S include SO_2 , H_2S , carbonylsulfide (COS), dimethylsulfide (DMS), carbon disulfide (CS_2), and methylmercaptan, as well as SO_4^{2-} and sulfite (SO_3^{2-}). Estimates for natural S emission rates range from 100 to 200 Tg SO_2/year (Tg = 10^{12} g), suggesting humans are responsible for roughly 40 to 60% of the S entering the atmosphere. Natural sources of S include volcanic activity and biogenic gases from terrestrial and ocean ecosystems as well as wetland, swamp, and other anaerobic environments. Coal-fired,

Table 7.1 Potential Environmental Impacts Due to Sulfur

Environmental Description of Problem Concern	
Acidic deposition	Sulfuric acid formation in the atmosphere results in wet deposition (rain, snow, mist, fog) and dry deposition (particulates and gases) that may be detrimental to vegetation, surface waters, buildings and structures, and humans; see Table 5.1 for environmental impacts due to N and Chapter 11 for further discussion on acidic deposition
Acid sulfate soils	Caused by the release of H_2SO_4 into the soil solution through the oxidation of sulfidic materials that are commonly associated with coastal regions and lignite coal mining operations (Fanning and Burch, 2002)
Acid mine drainage	Oxidation of reduced forms of S from mining activities produces H_2SO_4 that can have an impact on the soils or mine spoils and surface waters in the surrounding environments (Evangelou, 1998)
Sulfur toxicity to plants	High levels of SO_2 can enter plants through their stomatas; with oxidative conversion of the SO_2 , acid-forming substances can cause injury to leaves; additional formation of free radicals in chloroplasts impair metabolic function by inhibiting photosystem II, lipid peroxidation, and chlorophyll breakdown; H_2S is also phytotoxic and causes necrotic lesions and tip burn, as well inhibition of root growth, browning, and dieback (Hogan et al., 1998)
Sulfur toxicity to animals	Both ruminant and nonruminant animals can suffer from S toxicity; ruminants are susceptible to excess S in the forms of $(NH_4)_2SO_4$ and gypsum ($CaSO_4$) when these are used as nonprotein N or Ca feed sources, respectively; nonruminants are susceptible to excessive S amino acids, especially methionine, in their diet; livestock are also sensitive to H_2S (Goodrich and Garrett, 1986; Sweeten et al., 2003)
Geothermal activity	Geysers and other geothermal releases can bring significant amounts of gaseous and soluble S compounds to the Earth's surface; vegetation in the surrounding area can be killed by S gases or the extremely acidic soils that form; soil pH values as low as 0.9 have been reported in Yellowstone National Park, WY
Groundwater contamination	High SO_4^{2-} concentrations can render groundwaters unsafe for human and livestock consumption; hydrogen sulfide (H_2S) in groundwaters can be detected as a rotten egg smell (Fetter, 2003; Vance and Skousen, 2003)

electric-power-generating plants are the main anthropogenic source of S emissions, which was a concern that prompted the *1990 amendment to the 1970 Clean Air Act*. The United States and Europe, as well as several other countries, have seen a decline in S emissions since the 1990s, in part because of their clean air act regulations (Figure 7.1).

Industrial regions are the predominant source of anthropogenic S released into the atmosphere. A major environmental concern associated with atmospheric S release is *acidic deposition* (wet and dry deposition containing high levels of H_2SO_4), which has caused problems with vegetative growth, aquatic ecosystem acidification, human health, and structural deterioration that many nations throughout the world are now attempting to solve (see Chapter 11 for further discussion on acid deposition). Precipitation in affected areas can have a pH below 4, which, compared with rainfall in many nonindustrial areas with pH values of approximately 6, suggests a 100- to 1000-fold increase in H^+ ions in acidic precipitation.

The amount of S that falls annually in rainfall varies depending on outputs from natural and anthropogenic sources. Because plants require S (9 to 39 kg/ha each year for average crop yields), some regions benefit from the S added in rainfall. In some areas, atmospheric deposition of S may be sufficient to sustain adequate yields. For example, *S deposition* in the United States has been estimated for several urban (nonindustrial) and rural regions to be 1 to 37 kg S/ha in the Southeast, 4 to 42 kg S/ha in the Midwest, and 5 to 17 kg S/ha in the north-central states. Sulfur deposition in urban and rural regions of other countries is comparable to those listed above; 2 to 16 kg S/ha in Canada, 13 to 27 kg S/ha in China, and 10 to 20 kg S/ha in the former Soviet Union. In the midlands of England, atmospheric S inputs reached levels as high as 160 kg S/ha, causing negative impacts to

Table 7.2 1998 Global Sulfur Emissions (as Tg^a of SO₂) from Different Sources and Countries

Country	Fossil Fuel	Industrial Processes	Biofuel	Biomass Burning	Agriculture	Total
Oceania	1.0	0.5	— ^b	0.1	0.1	1.7
Japan	1.5	0.6	—	—	—	2.1
Canada	2.2	0.4	—	0.2	—	2.8
Southeast Asia	3.0	0.5	0.1	0.2	—	3.8
Middle East	5.1	0.5	—	—	—	5.6
Africa	3.9	1.3	0.6	1.2	—	7.0
South Asia	5.4	0.5	1.6	—	—	7.5
Latin America	4.9	4.4	0.1	0.7	—	10.1
Eastern Europe	8.9	1.6	—	—	—	10.5
Former USSR	13.0	3.0	—	—	—	16.0
OECD Europe	11.4	5.0	—	—	—	16.4
United States	17.1	1.0	—	—	—	18.1
East Asia	34.0	5.8	0.5	—	—	40.3
Total	111.4	25.0	2.9	2.5	0.1	141.9

^a Tg = 10¹² g.

^b Dash represents values below 0.1 Tg SO₂.

Source: Olivier, J. G. J. and Berdowski, J. J. M., in *The Climate System*, J. Berdowski et al., Eds., A.A. Balkema/Swets & Zeitlinger, Lisse, the Netherlands, 2001.

humans, plants, soils, and buildings, and resulted in S being labeled a “yellow poison.” Gaseous S species, SO₂ and H₂S, when present at high concentrations, can impair the growth of both plant leaves and roots.

Surface mining impacts on stream water quality result directly from the actual land disturbance. *Unweathered Earth materials* exposed to air and water at the surface during mining undergo rapid alterations and release many of their structural constituents, of which S is often a major chemical species, into water. When disturbed rock and soil are exposed to precipitation (e.g., rainfall, snow, hail, dew), water running off these materials carries solid particles (sediments) as well as dissolved constituents such as salts, metals, trace elements, and organic compounds that can pollute nearby surface waters. Water may also percolate into the disturbed materials causing movement and leaching of salts, metals, and trace elements into deeper levels, potentially resulting in groundwater quality impacts. The chemistry of the water is highly dependent on the chemistry of the overburden that was disturbed during the mining process.

Acid mine drainage is another environmental concern due to the mining of minerals such as coal, Cu, Zn, uranium (U), and others. After exposure of overburden materials during the mining process, oxidation and leaching can produce drainage waters that are acidic and that contain harmful concentrations of dissolved minerals. Nationwide, numerous rivers, streams, lakes, and reservoirs have been adversely affected by contaminated water draining from abandoned mines. The vast majority of these problem areas occur in the eastern United States where coal mine drainage is considered by the U.S. EPA to be the most significant nonpoint pollution problem. Wyoming is currently the leading coal-producing state in the country supplying approximately 40% of our nation's annual production, which is primarily due to the low S content of its coal and ease of extraction. Wyoming and other western states are also plagued with historic mining activities (e.g., mining that occurred in the 1800s) involving metal ores such as Cu, Pb, Zn, silver (Ag), and with the trace elements molybdenum (Mo) and U that were mined in certain regions. Surface water impacts from these mining activities include the generation of AMD from oxidation of pyritic ores

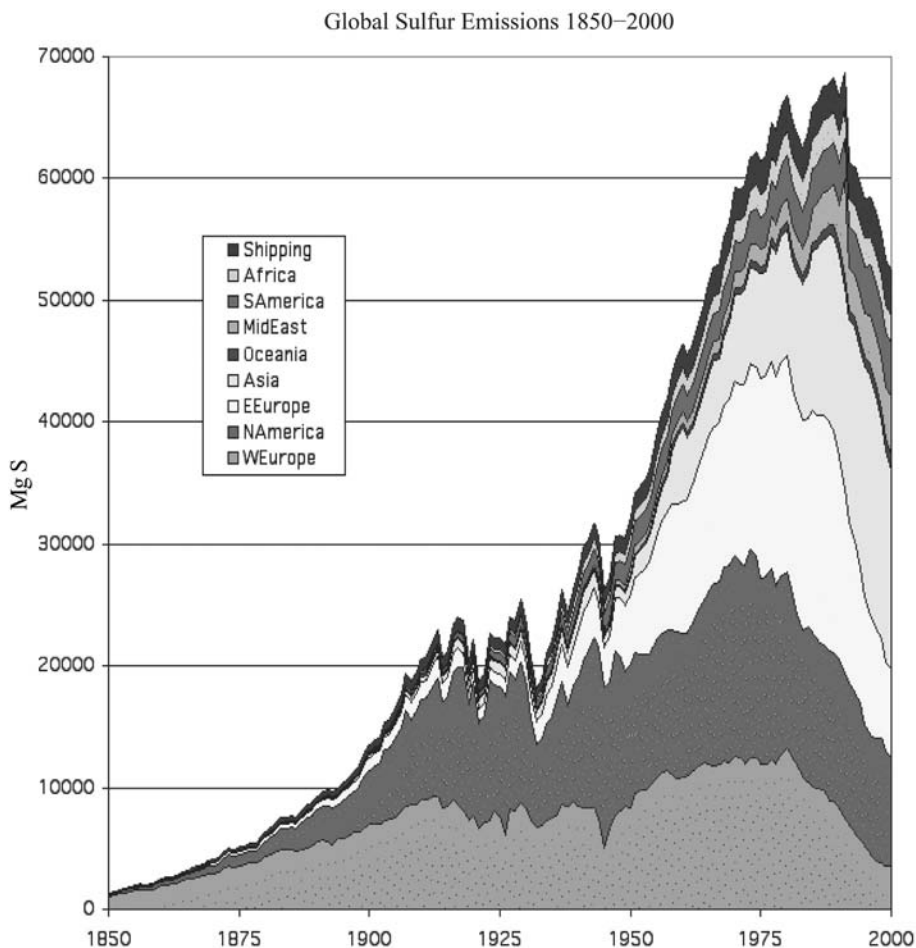


Figure 7.1 (Color figure follows p. 242.) Global sulfur emissions. Note the dramatic decline in emissions in the 1990s. (From David Stern's Web site <http://www.rpi.edu/~stern/datasite.html>. With permission.)

(e.g., iron sulfide, FeS_2). Other pollutants are also of concern including the metals aluminum (Al), antimony (Sb), cadmium (Cd), cobalt (Co), chromium (Cr), Cu, iron (Fe), manganese (Mn), Ni, Pb, and Zn, the trace elements arsenic (As), Mo and selenium (Se), the radioactive elements cesium (Cs), radium (Ra), thorium (Th), U and vanadium (V). In addition, mining operation by-products mercury (Hg) and cyanide (CN) may be released into the environment at high enough levels to be toxic to plants and soil and aquatic organisms.

Environmental Quality Issues/Events

Sulfur Origins and Contents of Major U.S. Coal Deposits

The S content of coal is related to its parent material (i.e., plant matter) and the sedimentary environment in which the coal formed. Low-S coal ($\leq 1\%$ S) is the result of incorporation of plant S into the accumulating peat that ultimately forms coal within a freshwater setting. Medium-S (>1 to $<3\%$ S) and high-S ($\geq 3\%$ S) coals are the consequence of two major sources of S, namely, that derived from

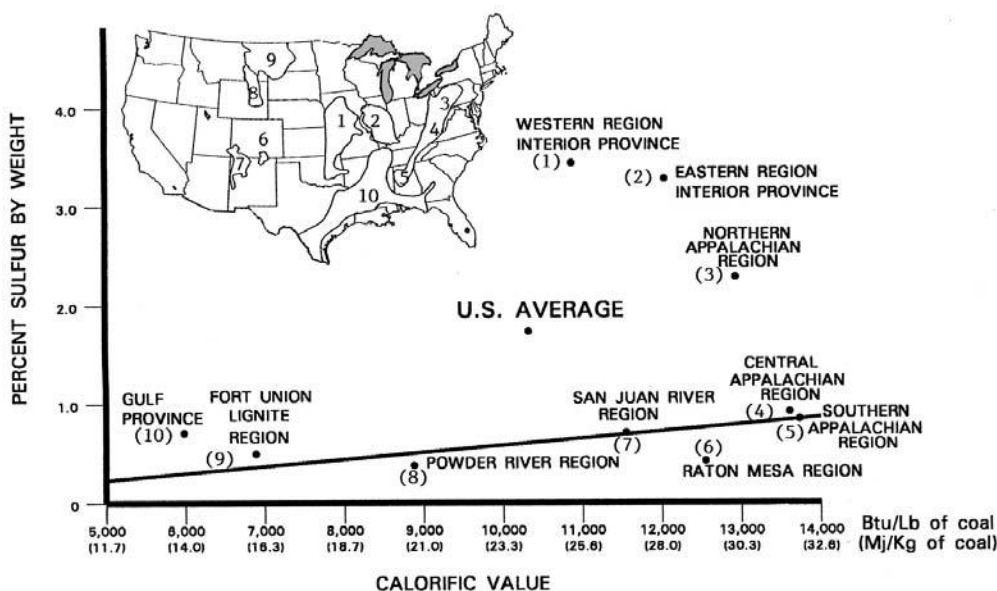
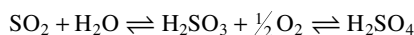


Figure 7.2 Average percent S content and heat energy (BTU/lb or MJ/kg) of major U.S. coal regions. The line represents the EPA compliance value of 1.2 lb SO₂ per million BTU output. (From <http://pubs.usgs.gov/of/1996/of96-092/index.htm>, verified 18 August 2004.)

parent plant material and SO₄-S in seawater that inundated the peat accumulation areas. High-S coals that can contain a significant amount of S, such as bituminous coal from Texas, are reported to have S contents as high as 8.9%. Geologic materials overlying coal deposits also contain S levels that parallel its abundance in the underlying coal. Acid mine drainage, therefore, is a greater concern in areas where high-S coals exist.

The major forms of S in coal are pyritic S, organic S, and SO₄-S, with pyritic and organic forms generally dominant. Pyrite is the sulfide (reduced-inorganic S) form and marcasite (FeS₂), pyrrhotite (Fe_xS_x), sphalerite (ZnS), galena (PbS), and chalcopyrite (CuFeS₂) are secondary sulfide sources. Several S-containing organic compounds are found in coal, including thiols, organic sulfides and disulfides, and thiophene and its derivations. Some of the organic S compounds may have been formed during the early stages of coal formation (humification process) when plant matter was decomposed by microbial activity. Only small amounts of SO₄-S minerals are present in coal, including gypsum (CaSO₄), barite (BaSO₄), and other Fe (FeSO₄) and sodium (Na, Na₂SO₄) minerals.

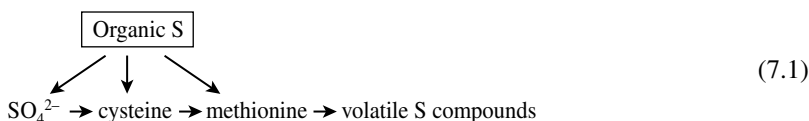
The high-S bituminous coals mined in Appalachian and north-central regions of the United States (see Chapter 11 for further discussion on coal combustion and emissions) have high heat energy (MJ/kg), but, due to their higher S contents (average 1 to 4% S contents, Figure 7.2), burning these coals results in the production of environmentally significant amounts of SO₂. Low-S sub-bituminous and lignite coals in the Rocky Mountain region have lower heat energy, but are mined extensively (more than 400 million Mg from Wyoming in 2004) because these materials are less harmful to the environment and are usually easier and cheaper to mine (i.e., low overburden-to-coal ratio). Sulfur dioxide produced from the combustion of coal reacts with water in the atmosphere to produce sulfurous (H₂SO₃) and sulfuric (H₂SO₄) acids according to the following simplified reactions:



— Based on Chou (1989)

7.3 GLOBAL SULFUR CYCLE

Sulfur exists in several inorganic and organic forms within the atmosphere, hydrosphere, and soil environments. Soil S exists as aqueous species such as SO_4^{2-} , solid forms that consist of mineral matter and organic constituents of plant, animal, and microbial origin, and gaseous species. Oxidation states for S range from -2 to $+6$ (see Table 7.3 for examples of oxidation states for inorganic and gaseous S species). As S cycles through atmosphere, hydrosphere, and soil ecosystems, several transformations can occur — due to biological, biochemical, and chemical processes — and form S species of different oxidation states. For example, COS, the most abundant atmospheric S gas, is oxidized to SO_4^{2-} or taken up by plants and metabolized. Sulfate entering soils is utilized by plants and microorganisms where SO_4^{2-} is reduced via metabolic pathways to amino acids, proteins, and other S-containing biochemicals. Decomposition of soil organic matter can release either oxidized or reduced S forms depending on environmental conditions. Several pathways have been proposed for the transformation of organic S to volatile S compounds including the following:



Physical processes, such as movement of S as dust, wet and dry deposition, or precipitation–dissolution reactions involving S evaporites (e.g., S minerals that form during desiccation), are also responsible for the transfer of S from one ecosystem to another.

The largest of the *Earth's S pools* (or reservoirs) is the lithosphere (metamorphic > sedimentary > igneous rock), followed by the hydrosphere (primarily oceans and seas), biosphere, and last the atmosphere, which contains only a minor amount of S (Figure 7.3). By far the greatest overall S

Table 7.3 Forms of Inorganic Sulfur in the Environment

Mean Oxidation State	Category	Compound	Formula
−2	Sulfides	Sulfide ion	S^{2-}
		Bisulfide ion	HS^-
		Hydrogen sulfide	H_2S
		Carbonyl sulfide	COS
−1	Polysulfides	Disulfide	S_2^{2-}
		Pyrite	FeS_2
0	Elemental	Sulfur	S^0
+2 ^a	Thiosulfate	Thiosulfate ion	$\text{S}_2\text{O}_3^{2-}$
		Bithiosulfate ion	$\text{H}_2\text{S}_2\text{O}_3$
		Thiosulfuric acid	
+4	Sulfites	Sulfite ion	SO_3^{2-}
		Hydrogen sulfite	HSO_3^-
		Sulfur dioxide	SO_2
+6	Sulfates	Sulfate ion	SO_4^{2-}
		Bisulfate ion	HSO_4^-
		Sulfuric acid	H_2SO_4

^a Sulfur oxidation states for thiosulfates are -2 and $+6$ with an average of $+2$.

Source: Stevenson, F. J. and Cole, M. A., in *Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients*, 2nd ed., John Wiley & Sons, New York, 1999.

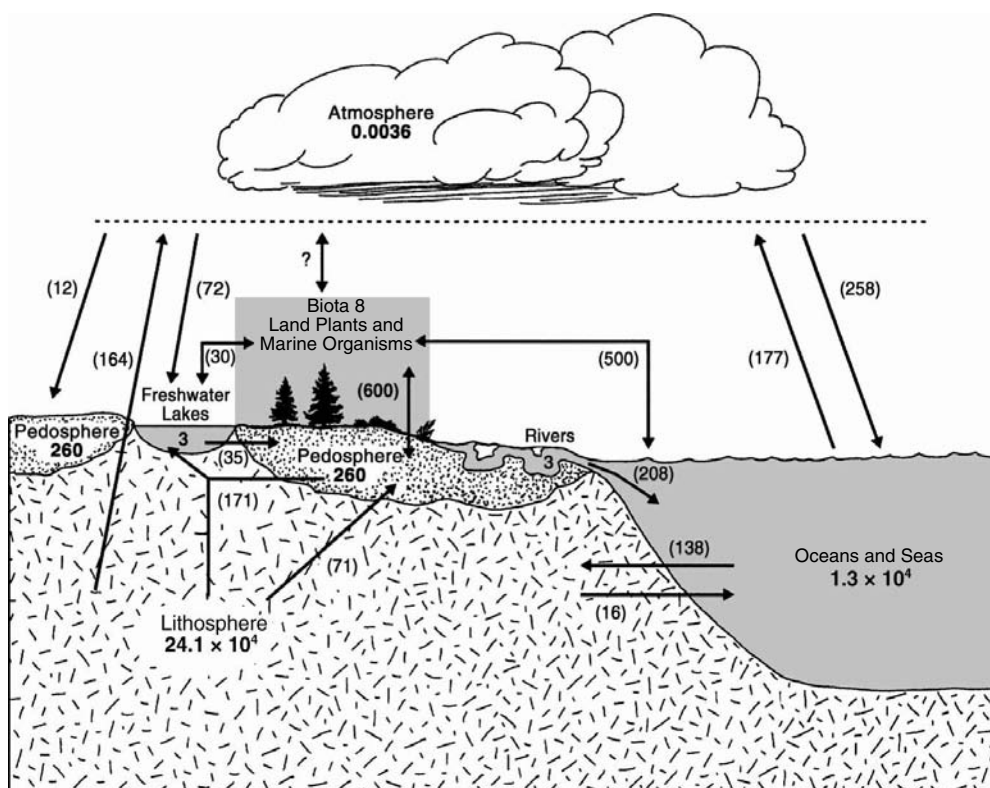


Figure 7.3 Environmental S pools and transformations (fluxes). Bold numbers represent pool concentrations (Gt = 10^{15} g or 1000 Tg) and flux rates are shown in parentheses (Tg/year). (Data from Trudinger, 1986.) An S balance (inputs = outputs) is presumed between the biosphere and atmosphere.

concentration exists in deposits associated with sedimentary pyrite, shale, and evaporite materials. In soils, S concentrations range from a low of approximately 0.002% in coarse-textured, highly weathered, leached soils in humid areas to greater than 5% in gypsiferous soils of arid and semiarid areas, and in coastal soils developed in tidal marshes. Soil S is predominately composed of inorganic and organic forms, and the ratio of the two varies with geomorphology, soil properties such as pH, moisture status, organic matter and clay contents, soil depth, and climatic conditions. Soil organic matter consists of approximately 0.5% S.

In the *S cycle*, transfer of S (the flux) from one pool (or reservoir) to another occurs at a rate proportional to the amount entering and exiting a pool (Figure 7.3). Although only small amounts of S are transferred from one S pool to another, humans have had an immense influence on the *annual atmospheric S flux*. As with the increase in C-based materials entering the atmosphere since the beginning of the industrial era (see Chapter 11), so too are S-based materials increasing. Over the past 100 years, the rate of S entering the atmosphere by mining and smelting operations and fossil fuel emissions has doubled; current S levels have, however, decreased as a result of laws enacted to reduce atmospheric S emissions. Over time, the amount of oxidized S is increasing, some of which is returned to the Earth's surface as wet and dry deposition (i.e., acidic deposition). Further discussion on atmospheric deposition of S and N can be found in Chapter 11; again, it should be emphasized that S deposition in the United States is actually lower now than during the early 1990s.

Example Problem 7.1

The atmospheric S MRT characterizes the transfer of S through the atmosphere and is calculated based on the size of the atmospheric S pool and the flux rate for wet and dry S deposition. The atmospheric S MRT is based on the assumption that the atmospheric S pool is representative of all locations, and that the flux rate is universal. Clearly, this is not the case in industrial areas and under variable climatic conditions. However, the concept is useful for examining the general characteristics of atmospheric S inputs and outputs.

$$\begin{aligned}\text{atmospheric S MRT} &= \text{atmospheric S pools/atmospheric S flux rate} \\ &= (3.6 \text{ Tg S}) / (342 \text{ Tg S/yr}) = 0.01 \text{ year} = 4 \text{ days}\end{aligned}$$

The primary S forms in wet and dry deposition are SO_4^{2-} and SO_2 , respectively. Specific atmospheric S compounds have MRTs that range from approximately 1 day for dimethyl sulfide ($(\text{CH}_3)_2\text{S}$) and H_2S to 160 days for COS, and are based on their concentrations, chemical reactivity, and chemical properties.

The soil S cycle is similar in many respects to N and P soil cycles in that each is affected by biological, biochemical, and chemical processes. The S cycle — emphasizing soil, plant, and animal S transformations — is shown in Figure 7.4. Four dominant S forms are found in soils, including *elemental S*, *sulfides*, *sulfates*, and *organic S compounds*. Additions of soluble S to soil results from mineral weathering, atmospheric deposition, fertilization (and other soil amendments), and decomposition of plant, animal, and soil organic matter. Losses of S occur during leaching, surface runoff, and crop removal. Transformations that take place between the various S forms are mediated primarily by biological and biochemical processes, which are discussed in more detail later in this chapter.

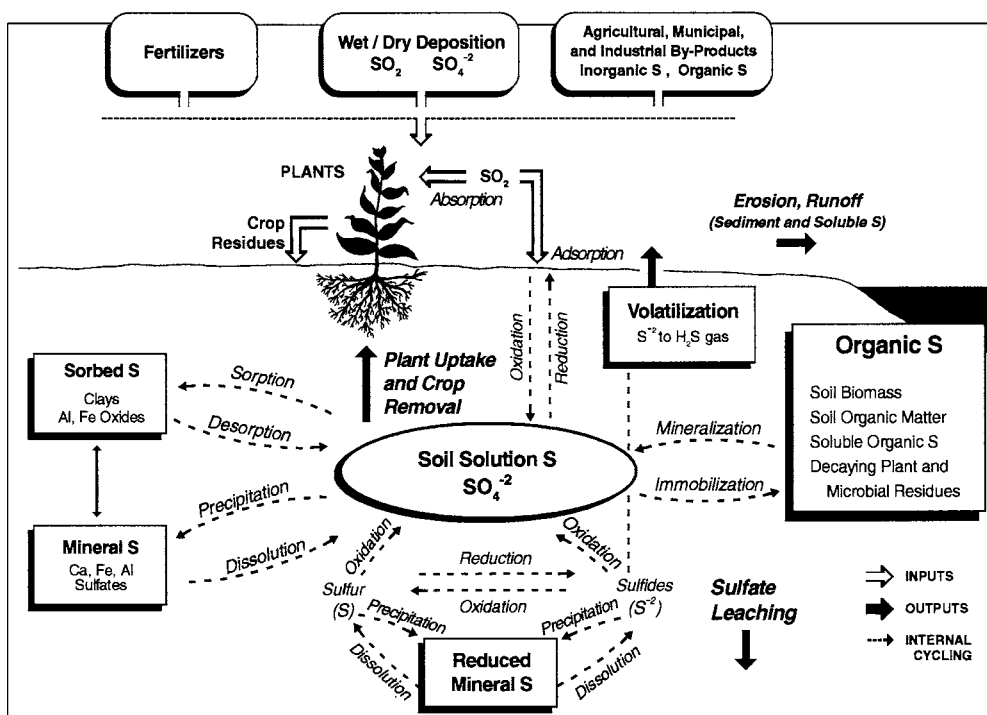


Figure 7.4 Environmental S additions, losses, and transformations that occur among and within atmosphere, biosphere, and soil systems.

7.3.1 Inorganic Sulfur in Soils

Several forms of *inorganic S* exist in soils (see Table 7.3). In well-drained soils, inorganic S occurs primarily as SO_4^{2-} in a dissolved, adsorbed, or solid state. Soils containing Al and Fe hydrous oxides are capable of adsorbing SO_4^{2-} and preventing losses due to leaching. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is found primarily in calcareous soils of arid and semiarid regions and may also occur as a coprecipitated mineral form associated with CaCO_3 (limestone). Other less common solid mineral forms of SO_4^{2-} include barite (BaSO_4), celestite (SrSO_4), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), and coquinbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$). In anaerobic soils such as wetlands, tidal marshes, and poorly drained soils, reduced forms of S are common and can include FeS , FeS_2 , H_2S , and S^0 .

Gaseous forms of S are also present in soils and range from trace concentrations in well-drained, aerobic soils to high concentrations in waterlogged, anaerobic soils. Soil S is less volatile than soil C and N compounds, whereas P has essentially no soil gaseous forms. Gases formed during organic matter decay that may be emitted from soils include carbon bisulfide (CS_2), COS, methyl mercaptan (CH_3SH), dimethyl sulfide ($(\text{CH}_3)_2\text{S}$), dimethyl disulfide ($(\text{CH}_3)_2\text{S}_2$), and H_2S , all of which have characteristic, distinctive odors. Sulfur emissions from anaerobic soils and wetlands (i.e., swamps) result in approximately 30 Tg S/year added to the atmosphere.

Elemental S and sulfides are oxidized to H_2SO_4 when exposed to aerobic conditions. Oxidation of reduced S occurs when subsurface geological materials are brought to the Earth's surface during mining activities or on draining tidal marshes. Under these conditions the solution pH level may be sustained as low as 2 or less until the reduced S is oxidized, neutralized, or otherwise removed from the soil/geologic environments.

Speciation of solution inorganic S is controlled by redox conditions (as measured by pe, electron activity or oxidation–reduction condition) and pH (H^+ activity) relationships as shown in Figure 7.5. Sulfate is the dominant species found at high pe levels (indicative of oxidized conditions) and all pH levels. At low to intermediate pe levels, sulfide species predominate, with H_2S at low pH (<7)

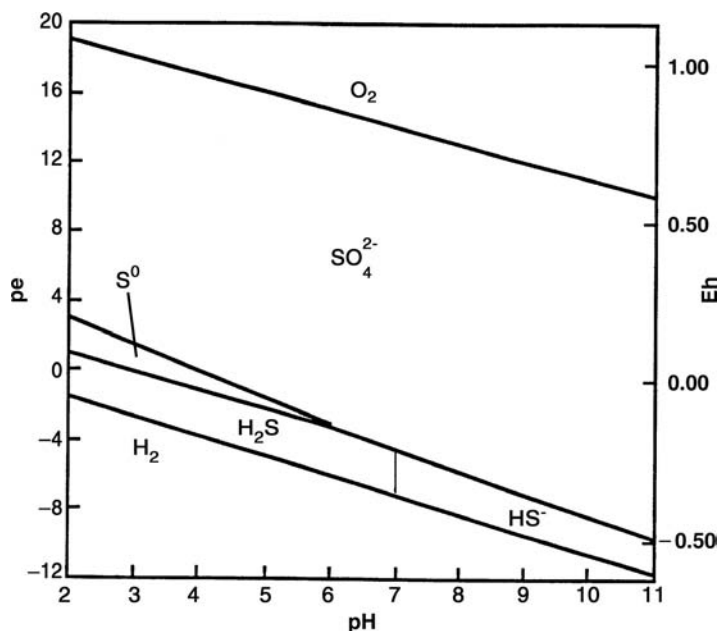


Figure 7.5 Relationship among the S species at different oxidation–reduction, e.g., redox (pe), conditions and variations in pH. The pH range is based on the most likely extremes found in soil ecosystems.

and HS^- at high pH (>7) levels; at extremely high pH levels (>11), S^{2-} is the dominant sulfide species. Elemental S can also exist at moderate pe levels and acidic pH values. Some S-containing amino acids are also stable at pe + pH levels within the SO_4^{2-} range, thus suggesting organic S compounds may persist in aerobic soil environments.

7.3.2 Organic Sulfur in Soils

Organic S is the dominant form of S in most soils and sediments. The distribution of S in several types of soils is listed in Table 7.4, which clearly shows that organic S is the predominant form of soil S in all but calcareous and possibly volcanic ash-derived soils. Generally, concentrations of inorganic S will only exceed organic S in low-organic-matter, calcareous soils typical of arid and semiarid regions. Further examination of the inorganic and organic S compounds can be obtained by S fractionation methods.

The content of organic S in soil and aquatic environments varies considerably, depending primarily on the amount of organic matter present. In soils, organic matter accumulates at the soil surface as plant materials decay; although subsurface horizons can also accumulate organic S (Table 7.5). Note in Table 7.5 that total and organic S in Soil 1 decrease with depth while inorganic S stays relatively constant, whereas in Soil 2 there is an accumulation of all three forms of S at the 30 to 60 cm depth. Soil 2 is typical of Spodosols (Podzols), which through translocation of organic matter into subsurface horizons have accumulated organic S. The increase in inorganic S is related to increased SO_4^{2-} sorption by Fe and Al hydrous oxides that accumulate in subsurface horizons of Spodosols.

Organic S compounds in soils and aquatic environments are derived from several plant, animal, and microbial sources. *Sulfur-containing amino acids* (cysteine, cystine, and methionine) are generally the most prevalent of the known organic S compounds, accounting for 10 to 30% of the total

Table 7.4 Total Sulfur and the Distribution of Inorganic and Organic Sulfur in Different Soils

Type of Soil	Location	Total S (mg/kg)	Inorganic S (%)	Organic S (%)
Agriculture	Queensland, Australia	11–725	2–18	82–98
	Iowa, USA	78–452	1–3	97–99
	New South Wales, Australia	38–545	4–13	87–96
	Brazil	43–398	5–23	77–95
	Alberta, Canada	80–700	8–15	85–92
	West Indies	110–510	2–10	90–98
	New Zealand	240–1360	2–9	91–98
Forest	New York, USA	68–2003	1–18	82–99
	Germany	74–328	7–28	72–93
	Illinois, USA	112–555	2–10	90–98
	Alberta, Canada	364–1593	2–10	90–98
	New Hampshire, USA	452–1563	1–8	92–99
	Maine, USA	81–2047	1–25	75–99
Surface	Iowa, USA	55–618	1–5	95–99
Organic	England	7405	5	95
Acid	Scotland	300–800	2–10	90–98
Volcanic ash	Hawaii, USA	180–2200	6–50	50–94
Calcareous	Scotland	460–1790	21–89	11–79

Sources: Freeney (1986), David et al. (1990), and Mitchell et al. (1992).

Table 7.5 Relationship of Total, Inorganic, and Organic Sulfur (mg/kg) by Depth in Two Soil Profiles

Depth (cm)	Total S		Inorganic S		Organic S	
	Soil 1	Soil 2	Soil 1	Soil 2	Soil 1	Soil 2
0–10	436	205	7	8	429	197
10–20	389	93	6	6	383	88
20–30	342	118	6	7	336	111
30–45	266	134	6	18	260	116
45–60	230	134	8	29	222	105
60–75	188	115	7	22	181	93
75–90	162	99	5	10	147	89

Note: Soil 1 is a Mollisol with decreasing organic matter with depth, and Soil 2 is a Spodosol with organic matter, Fe, and Al accumulations in the B horizons.

Source: Williams, C. H., in *Handbook of Sulphur in Australian Agriculture*, K. D. McLachlan, Ed., CSIRO, Melbourne, Australia, 1974.

S in various soils. These amino acids are readily decomposed and may only exist for short periods of time before they are utilized by microorganisms. In addition, S-containing amino acids are often bound to mineral and organic matter, making it difficult to extract amino acids from soils. Sulfur-containing polysaccharides and lipids are also present in soils and may comprise approximately 5% of the total S.

Municipal biosolids (sewage sludge) and animal manures contain several forms of organic S. Although these materials are perceived as waste products that require disposal, several benefits can be realized when utilizing biosolids and manures in a land application program (see Chapter 8 for more information on management of by-product materials). In addition to organic matter, municipal biosolids and animal manures also contain N, P, and both inorganic and organic forms of S. For example, some biosolids have been found to contain elemental S and sulfides, and organic S such as S-containing amino acids, alkyl benzene sulfonates, sulfonated acidic polysaccharides, and ester sulfates (a significant portion of which is derived from detergents).

7.3.3 Sulfur Fractionation

Because of the heterogeneous nature of organic matter (see Chapter 3), soil and aquatic organic S compounds are generally characterized by *S fractionation methods* that separate S into five basic fractions. Both inorganic S (SO_4^{2-} and nonsulfate S, primarily sulfides) and organic S (C-bonded and ester sulfate) that have been mentioned in the previous sections can be determined by these methods. Examples of the concentrations and proportions of the S fractions in municipal biosolids, soils, and lake sediments and waters are listed in Table 7.6. The S fractionation method can also be used to evaluate soil and aquatic S dynamics including transformations and flux rates.

The nature and content of soil S can be quite variable. By using an S fractionation method, total S is determined on a subsample of the soil. Water-soluble and phosphate-extractable S are also determined on subsamples, and the difference between the two is considered specifically adsorbed SO_4^{2-} (SO_4^{2-} sorption is discussed in Section 7.4.1). Inorganic nonsulfate S is evaluated directly by Zn-HCl digestion. Organic S comprises both *ester sulfate* ($-\text{C}-\text{O}-\text{S}-$) and C-bonded ($-\text{C}-\text{S}-$) forms with the former determined along with inorganic S through hydriodic acid (HI) digestion. *Carbon-bonded S* is obtained by difference (total S minus HI-digested S) because there is no method available that can accurately and completely account for all the C-bonded S in a sample.

Table 7.6 Average Sulfur Concentrations in Milligrams/Kilogram in Solid or Aqueous Samples from Different Ecosystems (percentages are given in parentheses)

Sample	Total S	Extractable SO ₄	Inorganic Nonsulfate S	Ester S	C-Bonded S
Municipal biosolids ^a (aerobic digestion)	11,000	1,180 (11)	1,480 (13)	4,040 (37)	4,300 (39)
Soil (<i>n</i> = 18) ^b					
O horizon	2047	N.D.	28 (1)	286 (14)	1,733 (85)
E horizon	95	5 (5)	3 (3)	19 (20)	68 (72)
B horizon					
0–2 cm	330	30 (9)	12 (4)	58 (18)	229 (69)
2–7 cm	320	42 (13)	11 (3)	46 (14)	221 (69)
7+ cm	256	45 (18)	9 (4)	43 (17)	159 (62)
B/C horizon	138	29 (21)	7 (5)	30 (22)	72 (52)
C horizon	81	11 (14)	9 (11)	18 (22)	39 (48)
Lake sediment ^a	7,320	1,130 (15)	60 (1)	1,450 (20)	4,680 (64)
Lake water (mg/L) ^a	2.05	1.7 (83)	0.00 (0)	0.22 (11)	0.13 (6)

Notes: Values in parentheses are the percent of total S in that S fraction. For lake water, values reported as mg/L. N.D. = Not determined.

Sources: ^aLanders, D. H. et al., *Int. J. Environ. Anal. Chem.*, 14, 245, 1983; ^bDavid, M. B. et al., *Soil Sci. Soc. Am. J.*, 54, 541, 1990.

The distribution of inorganic and organic S in several soils was shown in Table 7.4. Organic S, which consists of ester sulfate (Figure 7.6a) and C-bonded S (Figure 7.6b), is the dominant form of S in most soils. There appears to be a difference in the content of organic S forms in agricultural vs. forested soils. The percentage of total S in agricultural soils that is composed of ester sulfates ranges between 35 and 60%, whereas in forested soils the range is lower, from 20 to 30%. The amount of C-bonded S in forested soils typically averages 50 to 80% of the total S. In *agricultural soils*, higher percentages of ester sulfates, relative to *forest soils*, have been attributed to the removal of C-bonded S with cropping. The mineralization of organic S compounds follows different processes depending on whether it is a C-bonded or ester sulfate compound that is mineralized. For example, biological mineralization favors C-bonded S, whereas biochemical mineralization involves ester sulfate compounds. Additional information on S mineralization is presented in later sections of this chapter.

7.4 SULFUR RETENTION AND TRANSFORMATIONS IN SOILS

Several processes that occur in soil and aquatic environments affect S movement and transformations. The most important processes are sorption–desorption of SO₄²⁻, inorganic S oxidation–reduction, and organic S transformations. It was pointed out in previous sections that organic S comprises the greatest proportion of total S in most soils. Organic S transformations, therefore, are of particular importance when considering soil S cycling and reactions.

7.4.1 Sorption and Desorption of Soil Sulfate

Sorption of SO₄²⁻ by soils results in the retention of S that otherwise would have been leached from the soil profile. Because SO₄²⁻ is the major form of S that is taken up by plants, the retention of SO₄²⁻ may enhance the ability of a soil to supply S to plants in the future. The amount of water-soluble and exchangeable SO₄²⁻ can be low in some soils, and is dependent on factors such as soil type, climate, and management practices. The mineralogical composition of a soil can

that 1:1 clays adsorb greater amounts of SO_4^{2-} than do 2:1 clays; SO_4^{2-} is also adsorbed by *metal-organic complexes*.

Sulfate sorption is influenced by pH, amount and crystallinity of Fe and Al hydrous oxides, and the presence of organic matter. Maximum sorption of SO_4^{2-} occurs at low pH, typically around pH 3 to 4.5, which is due to a net positive surface charge that develops on Fe and Al hydrous oxides. The increasing number of *positively charged sites* with decreasing pH enhances SO_4^{2-} sorption; however, Fe and Al hydrous oxides are not stable at extremely low pH values and their dissolution will reduce the number of sorption sites available. Organic matter can effectively hinder SO_4^{2-} sorption by coating mineral and hydrous oxide surfaces or by competing with SO_4^{2-} for sorption sites.

Desorption of SO_4^{2-} may occur if soils have received high S inputs, have a relatively low SO_4^{2-} sorption capacity, or if SO_4^{2-} is displaced by competing anions. The amount of readily desorbable SO_4^{2-} decreases with time, which has been attributed to the formation of more tightly bound (specifically adsorbed) SO_4^{2-} or a conversion of the SO_4^{2-} to organic forms. Desorption of SO_4^{2-} is enhanced by using a phosphate-extracting solution that readily displaces SO_4^{2-} present in specifically bound forms.

Example Problem 7.2

Initial mass isotherms (see Chapter 3 for more information on sorption) were evaluated in a study examining dissolved organic carbon (DOC) and SO_4^{2-} sorption by Spodosol mineral horizons from Maine. By using a Tunbridge Bh soil horizon, the hypothesis that DOC interferes with the sorption of SO_4^{2-} was tested by conducting SO_4^{2-} sorption studies in the presence or absence of DOC. First, sorption studies were performed with SO_4^{2-} -only solutions; then similar concentrations of SO_4^{2-} were prepared with 67 mg C/L as DOC in each solution (Table 7.7). Sorption was calculated as follows:

Table 7.7 Sulfate Sorption, with and without DOC, by a Tunbridge Bh Horizon Characterized by the Initial Mass Isotherm Method

Initial SO_4^{2-} Solution per Sorbent (C_i) ^a (mg/kg)	Adsorbed SO_4^{2-} (mg/kg)	m^b	$-b^b$	RSP ^b	r^2
Sulfate Only Sorption Study					
0	-32	0.48	32	62	0.998
60	-7				
120	24				
240	90				
480	195				
Sulfate Plus DOC Sorption Study					
0	-63	0.45	61	111	1.000
60	-34				
120	-5				
240	45				
480	153				

Note: See Chapter 3 for details on the IM isotherm.

^a C_i equals the initial amount of sorbate (i.e., SO_4^{2-}) added with respect to sorbent concentration.

^b The IM isotherm (e.g., x/m (adsorbed or released SO_4^{2-}) = $mC_i - b$) characterizes the slope (m) and y intercept (b). Because native SO_4^{2-} sorbate levels are high in some soils, there are cases where SO_4^{2-} release occurs (i.e., when b is negative). The SO_4^{2-} reserve soil pool (RSP) can be calculated from $\text{RSP} = b/(1 - m)$ and is a measure of the labile SO_4^{2-} or an estimate of the potential level of biologically active SO_4^{2-} in the soil.

Source: Vance, G. F. and David, M. B., *Soil Sci.*, 154, 136, 1992.

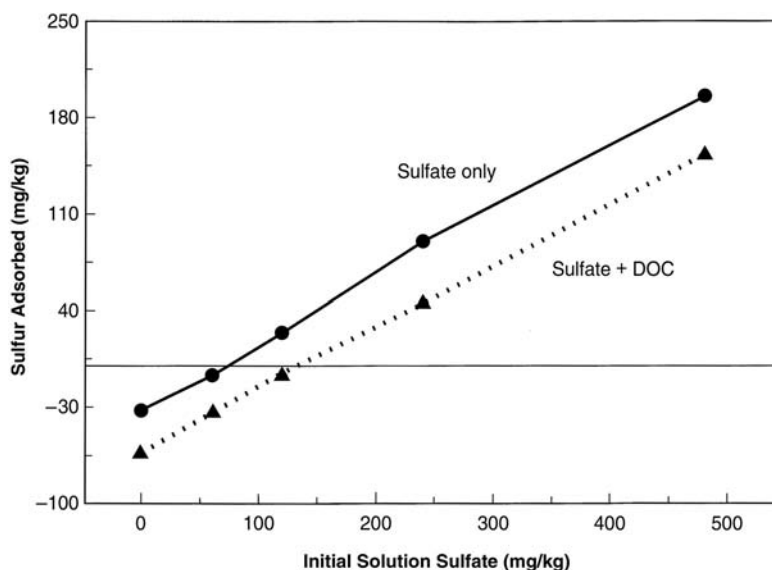


Figure 7.7 Sulfate sorption isotherms illustrating the influence of DOC on the amount of SO_4^{2-} adsorbed by a Spodosol (Tunbridge) Bh horizon. (Data from Vance and David, 1992.)

$$\begin{aligned}
 & (\text{SO}_4^{2-} \text{ initial} - \text{SO}_4^{2-} \text{ final}) \times (\text{volume of solution/soil wt}) \\
 & = \text{mass of } \text{SO}_4^{2-} \text{ adsorbed/mass of soil}
 \end{aligned}$$

where $\text{SO}_4^{2-} \text{ initial}$ and $\text{SO}_4^{2-} \text{ final}$ represent the amount of SO_4^{2-} added and that which is determined in the soil solution after reacting for a specified time, respectively.

Results of this study indicate DOC caused a reduction (i.e., lower b , intercept, and higher reactive soil pool, RSP, values) in SO_4^{2-} sorption due to competition for the adsorption sites; note that the slope (m) was not greatly influenced by DOC addition (Figure 7.7). The greater affinity of DOC for the adsorption sites may have been due to anion exchange, specific adsorption, and/or physical interactions between the soil and DOC.

7.4.2 Inorganic Sulfur Oxidation–Reduction Reactions

Oxidation–reduction (redox) reactions involving inorganic S are primarily mediated by soil microorganisms. The role of S redox reactions in soils was shown in Figure 7.4, which portrays several pathways available for the oxidation or reduction of S. As mentioned earlier, SO_4^{2-} is the dominant aqueous inorganic S form in aerobic soils. Sulfides are more important in anaerobic soils found in wetlands, swamps, and tidal marshes. Therefore, reduction reactions involving SO_4^{2-} and oxidation reactions involving S^{2-} are considered here.

Sulfate reduction occurs by *assimilatory* or *dissimilatory reduction reactions*. The assimilation reduction process occurs when microorganisms utilize SO_4^{2-} in the assimilation of cellular constituents. In converting inorganic S to organic S, the S is immobilized (see next section for a discussion of mineralization and immobilization processes). The dissimilatory reduction process is unique to a specific genera of bacteria (e.g., *Desulfovibrio*) that reduce SO_4^{2-} to sulfides. Dissimilatory SO_4^{2-} reduction occurs in anaerobic environments such as waterlogged soils, swamps, stagnant waters, and tidal marshes (Vasconcelos and McKenzie, 2000).

Conditions under which dissimilatory S-reducing microorganisms are capable of surviving are quite varied. They can live in soils with an extensive pH range and high salt content such as found

in saline lakes, evaporation beds, deep-sea sediments, and oil wells. A low redox potential (Eh) of less than 100 mV ($p_e = 1.69$) is required for their growth; under higher redox potentials, dissimilatory S-reducing microorganisms can persist in a dormant state.

Environmental problems associated with SO_4^{2-} reduction are varied. In municipal biosolid treatment systems, the production of H_2S leads to excessive corrosion of stone, concrete, and pumps as well as other components of the biosolid distribution system. Hydrogen sulfide also has an odor similar to that of rotten eggs. The presence of reduced forms of S in fossil fuels, sediments, and anaerobic soils can cause a number of problems, which will be discussed in the next section, as S oxidizes back to SO_4^{2-} .

Oxidation of *reduced inorganic S compounds* occurs under aerobic conditions and follows several pathways. Although S oxidation is considered to be primarily biologically driven, chemical oxidation of sulfides (S^{2-}), sulfites (SO_3^{2-}), and thiosulfates occurs readily in nature; however, the rate of chemical oxidation is slower than biochemical oxidation. Oxidation of reduced S is also an acidifying process, which is a cause for concern in certain situations. Examples of S oxidation that result in the formation of acidity are



There are several types of autotrophic and heterotrophic microorganisms capable of oxidizing S. Bacteria of the *Thiobacillus* genus can survive within a broad range of soil and environmental conditions; some *Thiobacillus* species are capable of living in soils with pH levels ranging from 1.5 to 9. *Sulfolobus* species are another group of S-oxidizing organisms that live in S-rich geothermal hot springs. They survive in waters that range in pH from 2 to 5 and temperatures of 60 to 80°C. Another form of S-oxidizing microorganisms that survives in hot springs is the *Thermothrix*, which, unlike *Sulfolobus*, grows in near-neutral pH waters.

In neutral and alkaline pH soils, the primary S oxidizers are often a group of heterotrophic microorganisms. The heterotrophic microorganisms of interest include several genus of bacteria (*Arthrobacter*, *Bacillus*, *Micrococcus*, *Mycobacterium*, and *Pseudomonas*), as well as some actinomycetes and fungi that are capable of oxidizing inorganic S compounds. These microorganisms are believed to oxidize inorganic S only as a consequence of other metabolic processes.

Factors that influence S oxidation in soils include soil type, pH, temperature, moisture, and organic matter. Oxidation of inorganic, reduced forms of S is an *acidifying process* that can result in acidic soils that are toxic to plants, animals, and microorganisms. Acid mine drainage occurs when reduced forms of S are oxidized during and after the mining process. Oxidation of pyrite, a common S-containing mineral found in reduced subsurface environments, can result in site degradation if toxic metal solubility reaches harmful levels that affect plants and aquatic organisms.

7.4.3 Organic Sulfur Transformations

Transformations of organic S to inorganic S and volatile gases are processes mediated by soil microorganisms. Release of inorganic S during the decomposition of organic matter (e.g., mineralization and oxidation) is important for supplying adequate S for plant growth. Soil factors that influence the growth and activity of microorganisms (e.g., pH, temperature, soil moisture, substrate availability) will also affect the rate of organic S transformations.

Transformations of organic S to inorganic S, and of inorganic S to organic S, are processes that describe S mineralization and immobilization, respectively, as shown in the following equation:



There are two processes involved in S mineralization: biological and biochemical. *Biological mineralization* is driven by microbial requirements for energy from organic C, for which S is released as a by-product of C oxidation to carbon dioxide (CO₂). Biological mineralization is generally more rapid with fresh organic matter substrates. *Biochemical mineralization* is the result of enzymatic hydrolysis of ester sulfates to SO₄²⁻. During biological mineralization of S, inorganic S — primarily SO₄²⁻ — is released as microorganisms decompose organic matter, utilizing some of the SO₄²⁻ to synthesize cell constituents and releasing some inorganic SO₄²⁻ to the soil solution. Immobilization of S is a process by which inorganic S is assimilated by microorganisms when low-S organic energy sources (i.e., organic matter) are added to soils. Mineralization–immobilization processes are also discussed for N and P in Chapters 5 and 6.

Rates of S mineralization are not proportional to the total amount of S in organic matter due to the variety of S-containing organic compounds in soils that have different decomposition rates, the type of plant and animal residues that affect *mineralization–immobilization rates and release*, and the formation of S-containing precipitates, e.g., CaSO₄, Al₂(SO₄)₃, that can influence the amount of plant-available S. The C:S ratio of these materials is extremely important because, in general, net mineralization occurs when the C:S ratio is less than 200:1, net immobilization occurs when the C:S ratio is greater than 400:1, and a steady state results when the C:S ratios are between 200:1 and 400:1.

7.5 SULFUR EFFECTS ON PLANTS

Sulfur is one of the *secondary plant nutrients* — S, Ca, Mg — but it has been considered by many as the fourth most important plant nutrient after N, P, and potassium (K). *Sulfur deficiencies* have become increasingly common as the use of fertilizers that contained S (e.g., normal superphosphate, ammonium sulfate) has been replaced by use of low-S fertilizers (e.g., triple superphosphate, ammonium phosphates); as S-containing pesticides have been converted to organic-based pesticides; and as atmospheric S inputs have been reduced — all of which have lowered the amount of S added to soils. Since the development of new high-grade fertilizers with low-S impurities, S deficiencies have become more evident in many parts of the world. Higher crop yields have also put a *greater demand on soil S reservoirs* to supply *extra amounts* of available S for increased plant growth. Reports of S deficiencies and increased crop yields due to S fertilization have been reported in several regions throughout the United States and in other parts of the world. Generally, S deficiencies are more likely in the Southern Hemisphere than in the Northern Hemisphere, and are also a greater problem in the tropics than in temperate environments.

Gaseous atmospheric S compounds may have a detrimental, beneficial, or neutral effect on plants. The concentrations of ambient gaseous S forms, SO₂ and H₂S, are low and can be beneficial; however, in the vicinity of high-discharge areas, the concentration of these ambient gases may be harmful to plants. Plants absorb SO₂ primarily through the stomata and are capable of oxidizing the SO₂ to sulfites and sulfates. When plants are exposed to levels of SO₂ that exceed the ability of the plant to oxidize sulfite to sulfate, sulfite can accumulate in the plant to toxic levels. Visual toxicity symptoms on affected leaves can be mistaken for other types of injury; noting the close proximity of an SO₂-generating source will help in diagnosing whether S toxicity has occurred. Short-term exposure of plants to H₂S generally causes little, if any, damage; however, continuous exposure to low H₂S concentrations, such as in the air near geothermal sites, may affect plants by causing leaf lesions, defoliation, and decreased plant growth.

7.5.1 Sulfur in Plant Nutrition

Sulfur requirements vary with plant species, cultivars, and stages of development. Several S-containing compounds are present in plants, but the majority of the S is part of the amino acids cysteine, cystine, and methionine, which are found largely in proteins. Additional S compounds include vitamins, biotin, thiamine, B₁, and other coenzymes such as lipoic acid and coenzyme A (CoA). Sulfur deficiencies not only reduce yields due to improper plant nutrition, but also lower the quality of certain crop products (e.g., digestibility of forages and baking quality of flours).

Various *S pathways* are involved in the synthesis of organic S compounds from SO_4^{2-} as illustrated in Figure 7.8. Once S (primarily SO_4^{2-}) enters the plant, it is activated through the formation of adenosine-5'-phosphate (APS); APS is a precursor to 3'-phospho-APS (PAPS), which is an intermediate in the formation of ester sulfates. The activated SO_4^{2-} in APS is reduced, and the reduced S is incorporated into either Fe-S proteins or as cysteine, which acts as a precursor to several organic S compounds (thiamin, lipoic acid, biotin, CoA, glutathione, and S-substituted cysteines). The majority of the two S-containing amino acids — cysteine and methionine — are incorporated into various proteins.

A number of *important plant metabolic functions* depend upon S-containing compounds. Methionine and cysteine are essential components to many plant enzymes and their structure and function are, in part, due to S interactions. The Fe-S protein ferredoxin is involved in redox reactions, most notably as a stable redox compound in the photosynthesis process. Nitrogen metabolism involving nitrate (NO_3^-) reduction, N_2 fixation, and NH_4^+ assimilation has been directly or indirectly related to S. Sulfur deficiencies can reduce symbiotic N_2 fixation, resulting in plant N deficiencies.

Sulfur deficiency is usually manifested through *visual symptoms* of light green to yellow leaves that appear first along the veins of young leaves. Legumes are particularly susceptible to S deficiencies and are often diagnosed as having *N-deficiency problems* because of the similarity in the symptoms. Alfalfa and canola, because of their high S requirements, can be very susceptible to S deficiency. In corn, S deficiencies are generally noted by yellowing of the newer leaves, whereas N deficiencies show up on the older leaves. Sometimes emerging plants will show symptoms of S deficiency (e.g., more uniform chlorosis than that which is caused by N deficiencies), but these symptoms diminish as roots extend into the subsoil and absorb SO_4^{2-} that has been adsorbed by clays and metal oxides.

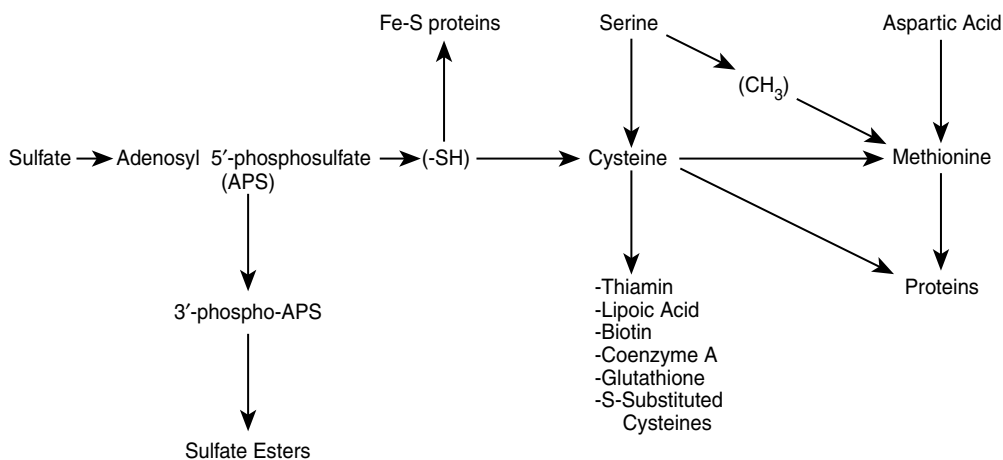


Figure 7.8 Pathways involving the transformation of SO_4^{2-} through intermediates to different S-containing organic compounds. The reduction of SO_4^{2-} in APS is denoted by $-\text{SH}$. (Adapted from Thompson J.F. et al., in *Sulfur in Agriculture*, M.A. Tabatabai, Ed., 1–22, 1986.)

7.5.2 Availability Index of Sulfur

Several methods are available to assess the status of S in soils and plants. However, there are no universal techniques for evaluating S availability in soils, or diagnosing S deficiencies in plants. It is well known that total S in soils is not a reliable test of S availability because much of the S exists in forms unavailable to plants. For soils, S availability is generally estimated by extracting the soil with water or solutions containing a salt, dilute acid, or phosphate (see Chapter 4, Environmental Testing). Depending on the nature of the extracting solution, information can be obtained on the soil content of (1) labile SO_4^{2-} ; (2) labile and adsorbed SO_4^{2-} ; or (3) labile and adsorbed SO_4^{2-} and portions of organic S. In addition to extraction methods, incubation techniques and microbial assays have also been used to estimate plant-available S.

Some commonly used techniques for *diagnosing S deficiencies* in plants include total S, SO_4 -S, ratio of SO_4 -S to total S, N:S ratio, and the Diagnosis and Recommendation Integrated System (DRIS). Total S levels in plants are generally an indication of soil S availability because plants acquire most of their S from soil solution SO_4^{2-} . However, several factors must be considered when interpreting plant total-S data because this varies with plant parts, age of plant and tissue, and interactions with other elements. Low, sufficient, and high total-S levels for a number of forages and agronomic crops are listed in Table 7.8. The amount of plant SO_4 -S can be used to estimate when S is deficient or in excess. A low plant SO_4 -S content would indicate SO_4^{2-} has been incorporated into organic S compounds, whereas high SO_4 -S contents suggest the plant is accumulating S. The ratio of SO_4 -S to total S is relatively independent of plant growth stage and may provide a better estimate of plant S requirements; the critical ratio is about 0.1. Total N:S ratios have also been used to estimate the status of plant S, but the ratio by itself does not indicate whether N or S is high or low.

In the *DRIS method*, several comparisons are made among indexes for different elemental ratios against established norm values. Three advantages to using the DRIS method are (1) analyses are independent of plant age and tissue; (2) nutrients are ranked in order of the most to the least limiting; and (3) nutrient balance is stressed. The DRIS method is a holistic approach to plant diagnostics, and the information derived from this method can be used to evaluate deficiencies of most of the

Table 7.8 Total Sulfur Contents in Various Forages and Agronomic Crops of Varying Levels of Sulfur Nutrition

Crops	S (%)		
	Low	Sufficient	High
Alfalfa	<0.25	0.25–0.50	>0.50
Barley	<0.15	0.15–0.40	>0.40
Clover, white	<0.25	0.25–0.50	>0.40
Corn	<0.25	0.25–0.80	>0.80
Cotton	<0.25	0.25–0.80	>0.80
Grass, brome	<0.17	0.17–0.30	>0.30
Oat	<0.15	0.15–0.40	>0.40
Peanuts	<0.20	0.20–0.35	>0.35
Soybeans	<0.20	0.20–0.40	>0.40
Sugarcane	<0.14	>0.14	—
Wheat, spring	<0.15	0.15–0.40	>0.40

Source: Jones, J. B., Jr. et al., *Plant Analysis Handbook: A Practical Sampling, Preparation, Analysis, and Interpretation Guide*, Micro-Macro Publishing, Athens, GA, 1991.

macronutrients and some of the micronutrients. Further discussion on the DRIS systems can be found in Walworth and Sumner (1987), Westerman (1990), and Jones et al. (1991).

7.6 MANAGEMENT OF SULFUR IN AGRICULTURE

As with N, P, K, Ca, Mg, and the micronutrients, S must also be managed to achieve a proper balance between deficiency and excess. Typically, *plant S needs* are similar to P requirements, with less than 15 kg S/ha required for average yields of grasses and cereal grains and between 15 and 35 kg S/ha for forage crops, sugar beets, cabbage, and cotton. Other plants remove as much as 90 kg S/ha. A *management program* must provide sufficient amounts of all plant nutrients to obtain economic yields while giving due consideration to potential environmental impacts. Unlike N and P, the agricultural role in S pollution of air and water is minimal, or nonexistent. Therefore, management of S in agriculture focuses more on supplying adequate amounts of S for crop production than on S impacts on the environment. Soluble SO_4^{2-} levels of approximately 20 mg/L in the soil solution are usually sufficient for most crops. When readily soluble SO_4^{2-} concentrations are less than 10 mg/L, S supplementation may be needed for proper plant growth. Coarse-textured, S-deficient soils will have SO_4^{2-} concentrations that are often less than 5 mg/L.

Example Problem 7.3

A 10-g soil sample is extracted with 0.025 L of calcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) by shaking for 2 h at room temperature. The sample is filtered (Whatman No. 42 filter paper) and the supernatant (filtered solution) analyzed for $\text{SO}_4\text{-S}$. Results suggest there are 2 mg $\text{SO}_4\text{-S/L}$ in the supernatant solution. Does this soil require additional S to produce an average yield of cotton that needs approximately 20 kg S/ha? An approximate relationship that is commonly used in determining requirements on a kg/ha basis is to assume that a hectare furrow slice (18 cm depth) is about 2,250,000 kg/ha, assuming a soil density of 1.3 g/cm³. From our analysis and the hectare furrow slice relationship, the amount of S needed is calculated as:

$$\frac{2 \text{ mg SO}_4\text{-S}}{\text{L solution}} \times \frac{0.025 \text{ L solution}}{0.010 \text{ kg soil}} = \frac{5 \text{ mg SO}_4\text{-S}}{\text{kg soil}}$$

$$\frac{5 \text{ mg SO}_4\text{-S}}{\text{kg soil}} \times \frac{2,250,000 \text{ kg soil}}{\text{ha}} = \frac{11,250,000 \text{ mg SO}_4\text{-S}}{\text{ha}} \text{ or } \frac{11.2 \text{ kg S}}{\text{ha}}$$

Based on these results, an additional 8.8 kg S/ha would be required.

Management of S for agricultural purposes is dependent on the properties of S and the factors that govern its availability. Figure 7.9 describes the various S inputs and S outputs that are generally part of an agricultural production setting. Inputs of S include crop residues, pesticides, animal manures, S in rainfall, fertilizers, mineral weathering, and organic matter mineralization to enhance the soil S supply. Outputs or losses of S include immobilization, volatilization, crop removal, leaching, and erosion. Preventing erosion, returning crop residues to the soil, and adding other sources of S (i.e., municipal biosolids, animal manures, and composts) will increase the amount of S in soils, in addition to supplying other essential plant nutrients.

No universal management plan can be designed for S because each situation warrants a close examination of the role S plays in both economic and environmental issues and controls. For

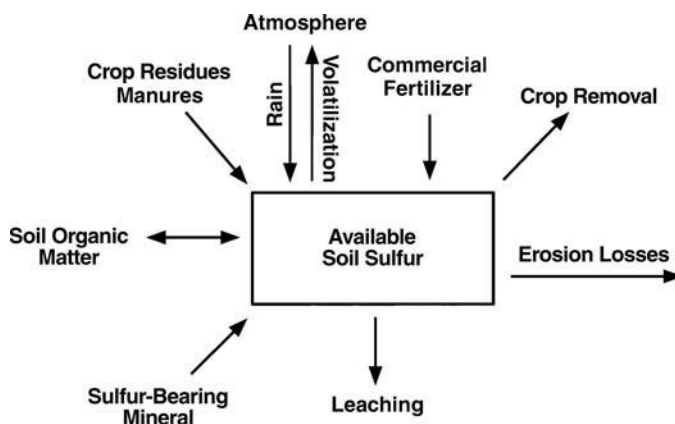


Figure 7.9 Example of S inputs and outputs in an agricultural ecosystem.

example, considering our current state of affairs with regard to acidic deposition, and its immense publicity, it is not surprising that any problem potentially associated with acid rain will warrant government action. The *1990 amendment to the Clean Air Act* has specifically designed regulations that call for a reduction in the amount of S that can be released to the atmosphere. Although acidic deposition has been shown to be detrimental, especially within areas surrounding the S-emitting source, atmospheric S contributions to crop S requirements have been a clear benefit to areas with lower-S soils.

7.6.1 Management of Sulfur in Cultivated Cropping Systems

Cultivation results in an initial mineralization of organic matter, releasing nutrients such as N, P, and S. Loss of S, as well as C, N, and P, is related to the intensity of cultivation, soil properties, and cropping practices, but usually ranges from 20 to 40% total S compared with uncultivated fields. As an approximate measure, about 1 to 3% of the soil organic matter will be mineralized each growing season. The amount of SO_4^{2-} released in the mineralization processes will depend on the nature of the organic matter, microbial assimilation, and biochemical processes. Predicting S needs is therefore difficult because most of the S in soils exists in organic forms that must undergo mineralization for the S to be released. Factors that affect the amount of plant-available S include temperature, pH, and moisture, all of which directly influence the growth and activity of microorganisms. If crop production uses less S than the amount of S mineralized, a net annual release of nutrients in excess of plant needs could result in a potential loss of S through erosion or leaching, and decreased availability of S to future crops. Therefore, it is important to use management practices that balance S needs.

There are many types of *S fertilizers*, several of which contain other essential nutrients. Examples include elemental S, K_2SO_4 , $(NH_4)_2S_2O_3$, $CaSO_4 \cdot 2H_2O$, and $MgSO_4 \cdot 7H_2O$, which will vary in their effect on soils as elemental S can cause acidification whereas neutral salts do not. The choice of one S-containing fertilizer over another should be determined based on cost when comparing fertilizers on an equivalent S basis. Factors that should be taken into consideration in S management programs include type of fertilizer S, timing of application, method of application, and placement. Both the physical and chemical characteristics of the fertilizer and soil will determine the best method and timing of application. Municipal biosolids and animal manures can also be used as a source of S. For example, the S content (dry weight basis) of biosolids ranges from 0.6 to 1.5%.

Criteria that can be used to determine the *economic benefits* of S fertilizer use include economic optimum S fertilizer rate, minimum S fertilizer rate, S fertilizer rate to maximize return on investment, minimum cost per unit of yield, and discounting future returns. All but the last criterion are based on present-year conditions such as cost of S fertilizer and additional expenses, expected yield, and anticipated return on investment. Discounting for future returns relies on additional benefits due to residual effects. These residuals may include S carryover, mineralization of other nutrients, or prevention of S deficiencies in perennial crops. In a long-term S management program, the latter strategy may be the most beneficial; however, on a short-term basis, the other economic criteria may result in increased profit margins.

7.6.2 Management of Sulfur in Grazed Systems

Grazed pastures and rangelands are different from cultivated croplands because most of the S is cycled through plants and returned to the soil as plant residues or animal excrement. The major S loss in grazed systems occurs when the animals are removed from the pasture or rangelands, or by fire, erosion, and disturbance events. Grazing animals can influence their environment by foraging, soil surface deformation (e.g., hoof action), selective eating habits, spreading undesirable weed species, and from excrement impacts. Grazing can also reduce plant photosynthetic area, which results in low C assimilation and translocation to plant roots (a process that increases the sequestration of C). Plant residue S is often retained in immobilized soil organic matter, with as much as 80% or more of S released from plant litter incorporated into soil organic S. Animals, however, enhance the process of plant decomposition and reduce the turnover rate of S cycled from soil through plants back to the soil.

Much of an animal's excrement, and in particular urine, provides a plant-available source of SO_4^{2-} . Domestic animals such as sheep and cattle produce *S-containing fecal excreta* that is proportional to the dry matter consumed; approximately 0.1 g S is excreted through fecal material per 100 g of dry matter consumed (Figure 7.10). The amount of S in urine varies based on the grazing environment, ranging from 6 to 90% with a value around 50 to 60% for pastures that contain sufficient S levels. Characterization of S forms in sheep indicated fecal matter contained 87 to 94% C-bonded S (C-S), 4 to 5% ester- SO_4^{2-} , and 1 to 14% inorganic S (1 to 4% as SO_4^{2-}), whereas urine contents are 10 to 14% C-S, 5 to 8% ester- SO_4^{2-} , and 80 to 85% SO_4^{2-} (Figure 7.10). Enhanced

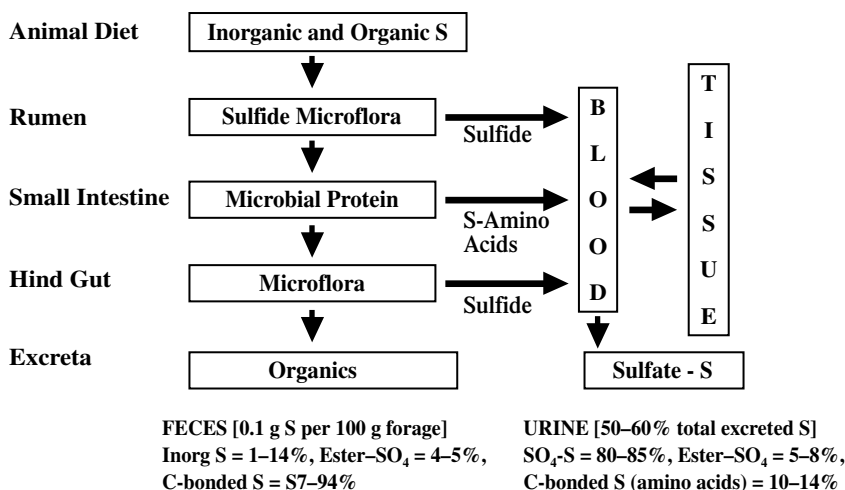


Figure 7.10 Sulfur transformations associated with ruminant digestion. Illustration and values are representative of sheep and cattle grazing on a S-sufficient pasture. (Adapted from Saggar et al., 1998.)

rates of S cycling are primarily attributed to urine due to high SO_4^{2-} levels that are more readily utilized by plants and microorganisms.

Application of S to grazed ecosystems is needed if S sources, such as atmospheric deposition, mineral weathering, or irrigation water (if used), are insufficient for plant growth requirements. Arid or semiarid environments with soils that are coarse textured, have low soil S reserves, and which have been intensively grazed are particularly susceptible to S deficiencies. Sulfur requirements are characterized by local soil and climatic conditions as well as land use practices. Added S is usually incorporated into organic matter with more of the S converted into *C-bonded S forms*; *ester sulfates* are more labile and can be rapidly mineralized by biochemical processes. Irrigation waters in some parts of the world may add sufficient levels of S to pastures and rangelands to support plant growth.

7.6.3 Sulfur in Forested Ecosystems

Because S is a *major tree nutrient*, there are important biochemical relationships that exist among the other tree nutrients, particularly N. Trees have the unique ability to accumulate S as SO_4^{2-} at rates greater than needed for N assimilation and protein production. In fact, N is taken up by trees at rates that are dictated by the amount of S available; thus, S determines the ability of trees to synthesize amino acids essential to proteins required for plant growth. This contrasts with agricultural crops that have the ability to accumulate $\text{NO}_3\text{-N}$, since both coniferous and broad-leaved trees do not store N even when S is limiting. Some research has shown that S additions do not directly improve the growth of trees, but rather increased improvement of the overall health of trees.

Total S and $\text{SO}_4\text{-S}$ requirements vary with different tree species, but levels of foliar $\text{SO}_4\text{-S}$ of 80 mg/kg and less are considered to indicate deficiencies. *Symptoms of S deficiencies* are often similar to N deficiency. Indication of S deficiency include overall yellowing of leaves and needles that is particularly evident at the base of needles, lesions and resin bleeding, and crown dieback. Fertilization of forests with N and P can result in a stress on available S, which is determined by the amount of soil solution SO_4^{2-} .

Atmospheric deposition of S and N has had positive and negative effects on forested ecosystems. Current research focuses on responses of forests to changes in atmospheric input because S levels are generally declining, whereas N concentration continues to increase or remains steady. A concern that relates to additional N inputs is based on how the forest ecosystem will respond over time. Some studies have shown that certain forest ecosystems are becoming *N saturated*, particularly forests in the northeastern United States, but Rocky Mountain forests are also showing initial signs of N saturation as well. Further discussion on atmospheric deposition of acidic S and N substances is presented in Chapter 11.

7.7 PROBLEM SOILS AND SURFACE WATERS

Salt-affected soils can have a wide pH range (Figure 7.11) and vary from acid-sulfate soils at low pH to Na-affected soils at high pH. Low-pH soils result from biotic and abiotic reactions involving reduced-S compounds. Gypsiferous soils (e.g., sodic soils) contain CaSO_4 , have low to high pH values ranging from 4 to 9, and are generally found in arid and semiarid environments. High-pH soils are the consequence of Na^+ salts contributing to alkaline hydrolysis reactions that result in poor soil physical conditions, inhibition to plant growth, and often inadequate water availability. Sulfur-containing minerals and compounds are important in the formation and reclamation of the low- and high-pH soils, respectively. In addition, the oxidation and mobilization of products from reduced-S-containing soils and mining materials can have a destructive impact on surface water quality.

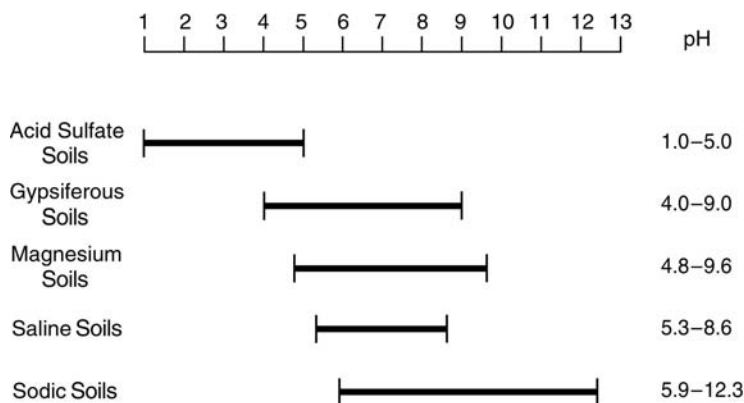


Figure 7.11 Range in pH values for different salt-affected soils. (Redrawn from Szabolcs, 1989.)

7.7.1 Acid Soils and Mine Spoils

When material containing reduced-S compounds is exposed to oxygen, high concentrations of H_2SO_4 can develop and form acid soils. Two examples where this might occur are (1) draining of coastal plains or tidal marsh sediments containing pyritic materials and (2) exposing pyritic materials to the atmosphere during mining activities. Reclamation of these areas requires the neutralization of both current (e.g., active, exchangeable, and nonexchangeable forms) and potential acidities that result when oxidation of reduced S occurs. Neutralization of the potential acidity is an important part of a reclamation program because over time reduced-S minerals will oxidize and contribute to the current acidity in soils. In most cases, the neutralization of potential acidity requires greater reclamation efforts to neutralize than active acidity. *Acid sulfate soils*, commonly referred to as cat clays, develop in drained coastal floodplains located mainly in temperate and tropical regions. If drained, the reduced-S compounds in these soils can oxidize to produce H_2SO_4 , which in turn can dissolve other minerals. Both acid sulfate soils and mine spoils can contain large amounts of pyrite (FeS_2) that, upon oxidation, can result in soil and water pH levels below 2.

Neutralization of some of the acidity produced during the oxidation of reduced-S compounds occurs when silicate minerals dissolve. However, during this process, high levels of potentially toxic metals such as Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn may be released. *Micronutrient deficiencies* involving Mo and boron (B) may occur in some vegetation due to the low solubility of these nutrients in acid soils. The survival and function of certain soil microorganisms (e.g., *Rhizobia*, mycorrhizae, and others) may be affected by acidity factors. *Reclamation* of acid soils and mine spoils requires addition of liming materials to neutralize all current and future acidity and the consideration of acid-tolerant crops. Soil tests should be done every 1 to 2 years, and the use of finely ground liming materials is recommended for faster acid neutralization. Reclamation efforts can turn unproductive soils into lands useful for crop production or rangeland use, in addition to alleviating a potential source of environmental pollution.

7.7.2 Acid Mine Drainage

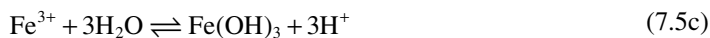
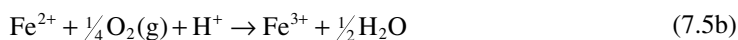
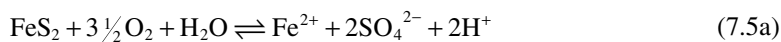
Acid mine drainage (AMD) occurs when certain sulfide minerals are exposed to oxidizing conditions and the resulting products are transported to surface waters such as streams, rivers, and lakes. Much of the AMD worldwide is associated with surface and underground mining activities, but acid drainage can occur under natural conditions or where sulfides in geologic materials are exposed by surface disturbances and subsurface excavations. The product of *pyrite oxidation* is an acidic, Fe-rich, and SO_4^{2-} -rich water. Detailed information on AMD reactions, control, and treatment is provided by Skousen and Ziemkiewicz (1995), Brady et al. (1998), and Evangelou (1998).

The *Surface Mining Control and Reclamation Act* (SMCRA) of 1977 specifies policies and practices for reclaiming areas after surface mining to minimize water quality impacts and to encourage the development of stable, diverse plant communities. Both the *Clean Water Act* (CWA) of 1977 and previous water control legislation (*Federal Water Pollution Control Act*, FWPCA, of 1972) propose enforcement that requires restoring and maintaining the chemical, physical, and biological integrity of our nation's water. The intentions of these laws were to establish a framework for permitting and regulating all point discharges into surface waters, particularly targeting the discharge of municipal biosolids, effluents, and other wastewaters from communities into streams, rivers and lakes. SMCRA was designed to place limits or standards on water discharged into the waters of the United States in order to maintain drinking water and recreational uses, and to restore the quality of degraded streams and lakes. The law has been interpreted as requiring all waters to be "fishable and swimmable."

Water discharged from surface mines is regulated by the CWA, and all mines are required to discharge only water that meets CWA effluent standards. Therefore, all water that comes from a permitted mine (whether the water was received as rainfall, snow, hail, at the surface, or from underground seepage) must pass through a sedimentation or treatment pond and meet or exceed discharge standards before it can be released into receiving surface waters.

Many areas in the United States and other parts of the world were disturbed prior to the enactment of any laws regulating their drainage quality and water release into streams. These disturbed areas may contribute significant amounts of pollutants to surface waters because they often are devoid of minimum vegetative cover and because their soil properties limit natural reclamation of the site. *Pre-1977 mining activities* were also considered in SMCRA legislation with provisions supporting reclamation of "abandoned" mined lands. These are surface mining disturbances that occurred prior to enactment of the law and where no individual or company is held responsible for the damaged land. Drainage from these surface mining operations has had and continues to have a dramatic effect on surface water quality. Many of these "abandoned" pre-1977 sites discharge AMD into surface water bodies such as rivers, streams, creeks, impoundments. Money generated since 1977 by the "abandoned mine land reclamation fund" and used to reclaim abandoned areas addresses the improvement of water quality from abandoned mine sites.

The *primary Fe sulfides* that produce AMD are pyrite and marcasite (FeS_2), with secondary sources chalcopyrite (CuFeS_2), covellite (CuS), and arsenopyrite (FeAsS) (Table 7.9). Acidity levels, metal composition, and metal concentrations in AMD depend on the type and amount of sulfide mineral and the presence or absence of alkaline materials. In areas where sulfides are present, the oxidation of Fe disulfides and subsequent conversion to acid occur through several reactions. The following chemical equations describe the processes involved in the *oxidation and acidification reactions* associated with reduced S transformations.



Initially, Fe sulfide is solubilized (Equation 7.5a) and ferrous iron (Fe^{2+} , reduced Fe), sulfate (SO_4^{2-} , oxidized S), and acid are formed. Ferrous iron is then oxidized (Equation 7.5b) to form ferric iron (Fe^{3+} , oxidized Fe). Ferric iron may be hydrolyzed and form ferric hydroxide, $\text{Fe}(\text{OH})_3$,

Table 7.9 Important Metal Sulfides in Geologic Subsurface Environments

FeS ₂	–	Pyrite	MoS ₂	–	Molybdenite
FeS ₂	–	Marcasite	NiS	–	Millerite
Fe _x S _x	–	Pyrrhotite	PbS	–	Galena
Cu ₂ S	–	Chalcocite	ZnS	–	Sphalerite
CuS	–	Covellite	FeAsS	–	Arsenopyrite
CuFeS ₂	–	Chalcopyrite			

and H⁺ acidity (Equation 7.5c), or directly attack pyrite and act as a catalyst in generating more Fe²⁺, SO₄²⁻, and acidity (Equation 7.5d). Under many conditions, Equation 7.5b is the rate-limiting step in pyrite oxidation due to the slow conversion of Fe²⁺ to Fe³⁺ at pH values below 5 under abiotic conditions. However, Fe-oxidizing bacteria, principally *Thiobacillus ferrooxidans* (an acidophilic chemolithotrophic organism), greatly accelerate the oxidation of Fe²⁺; bacterial activity is believed to be crucial for generation of most AMD (Evangelou, 1998).

If any of the reactions described above are limited, the generation of AMD would be slowed or possibly cease altogether. Removal of O₂ and/or H₂O from the system (two of the three *principal reactants*) would suppress pyrite oxidation. Almost complete absence of O₂ occurs in nature where pyrite forms; under these conditions, the pyrite remains almost completely unreacted. The rate of pyrite oxidation depends on numerous variables, such as reactive surface area, form of pyritic S, O₂ concentrations, solution pH, catalytic agents, flushing frequencies, and presence of *Thiobacillus* bacteria. The possibility of identifying and quantifying the effects of these and other controlling factors with all the various rock types in a field setting is unlikely. However, when pyritic material is fractured and exposed to oxidizing conditions, such as during mining operations or other major land disturbances, pyrite solubilization and leaching can result in reaction products (Fe and other metals, SO₄²⁻, and acid) migrating into surface water and groundwater sources.

The *drainage quality* (acid or alkaline) emanating from underground mines or backfills of surface mines is dependent on the acid (sulfide) and alkaline (carbonate) minerals contained in the disturbed geologic material. Alkaline mine drainage is water that has a pH of 6.0 or above and contains alkalinity; alkaline mine drainage may still contain dissolved metals that can create acidity by reactions described in Equation 7.5b and c. In general, sulfide-rich and carbonate-poor materials are expected to produce acidic drainage. In contrast, alkaline-rich materials, even with significant sulfide concentrations, often produce alkaline drainage waters.

The *natural base content* (alkali and alkaline earth cations, commonly present as carbonates or exchangeable cations on clays) of overburden materials is important in evaluating the future neutralization potential (NP) of the materials. The amount of *alkaline material* in unweathered overburden may be sufficient to overcome the acid-producing potential of reduced-S materials. Of the many types of alkaline compounds present in rocks, carbonates, specifically calcite (CaCO₃) and dolomite (CaMg(CO₃)₂), are the primary alkaline compounds that occur in sufficient quantities to be effective impediments to AMD generation. Higher alkalinities also help control bacteria and restrict the solubility of ferric iron (Fe³⁺), which are both known to accelerate AMD generation.

7.7.3 Sodic Soils

Soils of the arid and semiarid regions of the world can accumulate appreciable amounts of S-containing salts. However, *sodic soils* have an *exchangeable sodium percentage* (ESP) of 15% or

greater and low soluble salt concentrations (<4 dS/m) that result in a greater influence by sodium (Na^+) ions. The equation that is used to calculate ESP is as follows:

$$\text{ESP} = \frac{[\text{exchange Na}]}{\text{CEC}} \times 100 \quad (7.6)$$

where CEC = *cation exchange capacity*.

Under ESP conditions of 15% or greater, soil generally has a pH of 8.5 to 10 and excess Na^+ causes dispersion of clays, a reduction in soil pore diameter, destruction of soil structure, and decreased soil water permeability. In addition to the major influence of Na^+ on soil physical properties, Na^+ can also be toxic to certain plants when other cation concentrations are low.

Reclamation of sodic soils can be expensive if there is little or no water infiltration and permeability is very slow. The exchangeable Na^+ must be replaced by other cations, preferably Ca^{2+} , which is divalent and readily replaces Na^+ . Gypsum (CaSO_4) is very soluble and once dissolved can supply the necessary Ca^{2+} needed to displace Na^+ . An application of several megagrams per hectare of gypsum may be required to supply enough Ca^{2+} . The amount of gypsum required (GR) for reclamation can be approximated from the ESP and CEC of the sodic soil.

Example Problem 7.4

If a sodic-affected area has an ESP of 25% and a CEC of 20 cmol_c/kg, and the goal is to lower the ESP to 5%, the *gypsum requirement* (GR) would be calculated as follows:

$$\text{GR} = (\text{Na}_x) \times 4.5 \text{ Mg/ha to a depth of 30 cm}$$

where Na_x represents the cmol Na^+ /kg to be replaced (i.e., 20% of 20 cmol/kg). The 4.5 value is a constant that takes into consideration the equivalent weights for Na^+ and Ca^{2+} exchange, an assumed bulk density of 1.35 g/cm³, and a 70% efficiency factor. Therefore, the GR for the example given is determined as:

$$\text{GR} = 4 \times 4.5 = 18 \text{ Mg/ha}$$

A total of 18 Mg of gypsum/ha will be required to replace the 4 cmol Na^+ /kg. For best results, the gypsum should be incorporated into the surface and subsurface soil and adequate water, if available, should be applied after gypsum incorporation to leach out the Na^+ that is displaced by Ca^{2+} ions.

Materials containing reduced-S forms can also be used to reclaim sodic soils. Upon incorporation into sodic soils, reduced S will readily oxidize and produce sulfuric acid that lowers soil pH. Amounts of different S-containing materials required to reclaim sodic soils, using gypsum as the standard, are 0.18 for elemental S, 0.57 for H_2SO_4 , 0.75 for lime-sulfur, and 1.62 for iron sulfate. Thus, for every Mg of gypsum calculated from the GR equation, 0.18 Mg of elemental S or 1.62 Mg of iron sulfate would be needed.

For *salt-affected croplands* that utilize irrigation, a leaching requirement or leaching fraction needs to be determined to control salt and Na^+ problems. The leaching requirement is determined based on the amount of water needed to produce sufficient drainage, and is related to the salinity of both the irrigation and drainage waters. The *leaching requirement* (LR) is calculated as:

$$\text{LR} = \frac{\text{volume of drainage water}}{\text{volume of surface-applied water}} = \frac{\text{irrigation water salinity}}{\text{drainage water salinity}} \quad (7.7)$$

An acceptable salinity level is based on irrigation water costs, crop product value, and the sensitivity of the crop to salt. Salt-tolerant crops do not require as much leaching and can survive under higher salt conditions. For example, halophytes are plants that have adapted to salt-affected conditions; however, halophytes are normally nonagricultural crop species.

7.7.4 Coal Bed Methane Co-Produced Water

Natural gas is an important energy source in the United States. *Coal bed methane* (CBM) has only recently evolved as an important source of natural gas, currently accounting for about 9% of U.S. natural gas production. Unlike traditional natural gas, CBM is recovered by pumping water from coal seams, thus reducing water pressure and allowing the gas to desorb from the coal and migrate to the well bore. Coal bed methane production has increased dramatically since the 1980s because of economic incentives, simplicity in developing CBM wells, and low costs associated with start-up expenses. Although extensive CBM production has occurred in many regions, CBM activities in the Powder River Basin (PRB) in Wyoming and Montana are currently the most active in the United States. There are more than 20,000 CBM gas wells either permitted or drilled within the PRB, with estimates ranging from 50,000 to 100,000 new wells to be drilled in the future.

A primary concern with the PRB development of CBM is related to the water that must be removed to access the natural gas — a single CBM well typically produces from 4 to 100 L/min. Water coproduced with CBM is in a reduced state, dominated by Na^+ , HCO_3^- , and/or chloride (Cl^-) depending on the depositional setting of the individual coal seam. CBM water in the PRB is dominated by ions of Na^+ and HCO_3^- . *Water quality ranges* include pH from 6.8 to 8.0, salinity (EC) levels from 0.4 to 4.0 dS/m, sodium absorption ratios (SAR or the ratio of Na^+ to Ca^{2+} and Mg^{2+}) from lows of 5 to extreme highs of 70, which is well beyond the irrigation water suitability limit of 10.

Coal bed methane water management choices are influenced by factors such as cost, permitting, and environmental impacts. Some CBM waters are currently being used for land application on rangelands and for production agriculture; however, direct land application of saline-sodic, high-bicarbonate (HCO_3^-) CBM waters can potentially cause permanent damage to the native soils and vegetation. Application of CBM waters with high salinity (EC) can result in reduced water uptake and water stress to plants due to increased energy requirements for plants to obtain soil water. While tolerance to salinity varies among crop types, it is generally accepted that saline conditions have negative impacts on all crops at some level of salinity. Under saline conditions, some ions have toxic effects (e.g., Cl, Na, B) on plants. At higher pH, availability of micronutrients such as Fe, Cu, Zn, and Mn will be reduced. In addition to the above, salinity can affect soil physical properties. Salinity increases flocculation of clay particles resulting in aggregation, increased permeability and aeration, and better root growth and penetration. However, sodicity has the opposite effect on soils. Sodium causes dispersion of soil clay particles and organic matter, resulting in surface crusting, reduced infiltration, and reduced hydraulic conductivity. Clay soils are more vulnerable to sodicity than sandy soils and, because of crystal lattice structure differences, smectitic clays are more vulnerable than kaolinitic clays. Changes in soil physical and chemical properties associated with increased sodicity could, when coupled with poor vegetation cover, alter the resistance of soil to water and wind erosion, thus aggravating the problem caused by application of saline-sodic CBM water.

Coal bed methane producers have developed *management programs* that include water and soil amendments and treatments such as adding reduced-S and gypsum (CaSO_4) applications to prevent problems that might occur due to pH changes, calcium carbonate (CaCO_3) formation, and Na^+ dispersion and toxicity. Methods for application of CBM water include center-pivot and side-roll irrigation systems, portable water canons, and misters. Complex site-specific environmental factors such as topography, land use, soil types and quality, soil hydrologic characteristics,

water quality and application rates, and vegetation types and tolerances are considered when determining site-specific application methods, although nonenvironmental factors such as equipment installation and operating costs, landowner agreements, and regulatory environment are also important.

Environmental Quality Issues/Events

Acid Mine Drainage in the Appalachian Coal Region: Extent and Controls

In 1995, the EPA compiled a database of Maryland, Ohio, Pennsylvania, Virginia, and West Virginia streams with fisheries affected by AMD (Figure 7.12). The EPA database defined two levels of *stream impacts*: (1) streams with severe impacts were characterized as having “no fish,” and (2) streams with less severe impacts were described as containing “some fish” but where AMD had reduced the number of species or reduced their productivity. The EPA study indicated that more than 8230 km of streams were affected by AMD in the five-state area, with Pennsylvania containing more than 60%, or 5212 km, of the streams listed in the survey.

Most of the AMD in the Appalachian coal region (estimates are from 80 to 90%) comes from abandoned mines where no individual or company is responsible for the *poor-quality drainage*. Therefore, these streams will remain affected by AMD unless some state or federal agency, or a watershed organization, takes measures to improve the stream quality. While federal and state agencies or watershed organizations cannot afford chemical treatment (see below), passive treatment systems and land reclamation activities can reduce the acidity and metal load into streams from abandoned surface mines or underground mines. Significant reductions in acid loads to streams were found after land reclamation, and the acid load reductions were due both to reductions in water flow from the site and reductions in acid concentration in the water.

Passive systems, including wetlands, anoxic limestone drains, vertical flow wetlands (SAPS), and open limestone channels, have been constructed on many sites and have demonstrated measurable decreases in acid load to streams. These systems are low maintenance and do not require continual addition of chemicals; they remove metals from AMD by oxidation and precipitation processes, microbial reduction reactions, and sorption–exchange reactions. Longevity of system effectiveness is not entirely known for all systems, but passive treatment is an option for many stream restoration projects. On current mining operations, operators must mine in a responsible manner to restrict the production of AMD on their site. If AMD is produced during or after mining, they must develop a system for treating the water to be in compliance with water quality discharge limits.

In the Appalachian coal region, recommended reclamation procedures have included segregating and placing *acid-producing materials* above the water table and then treating, compacting, and covering the materials to reduce surface water infiltration. Another possible alternative is to re-mine areas where AMD comes from underground mines. An evaluation of ten re-mined sites in Pennsylvania and West Virginia showed that all were reclaimed to current standards, thereby eliminating mine portals and previously constructed highwalls, covering refuse, and revegetating the entire area. All sites also had improved water quality and some completely eliminated onsite AMD. At a surface re-mining operation of an underground mine in Preston County, WV, alkaline overburden (15,000 Mg/ha) from an adjacent surface mine was used for neutralizing acid materials on the re-mined site. Water quality from an acid-producing deep mine prior to re-mining had an average pH of 3.7 and 75 mg/L acidity as CaCO_3 , but after re-mining and reclamation, the pH was greater than 7.0 with no acidity.

Costs have been developed for five *AMD treatment chemicals* under four sets of flow (Lpm) and acidity concentration (mg/L as CaCO_3) conditions in an effort to help coal operators choose the most appropriate chemical for treating AMD (Table 7.10). These conditions are (1) 189 L/min flow and 100 mg/L acidity; (2) 3780 L/min flow and 100 mg/L acidity; (3) 945 L/min flow and 500 mg/L acidity; (4) 3780 L/min flow and 2500 mg/L acidity, which represent a sufficiently wide range for valid comparison for treatment systems. The net present value (NPV) is the value of the total treatment system plus annual operating and chemical expenses over the specified duration of treatment. A rate of 6% per year was used

Streams with Fisheries Impacted by Acid Mine Drainage in MD, OH, PA, VA, WV

(Based on EPA Fisheries Survey — 1995)

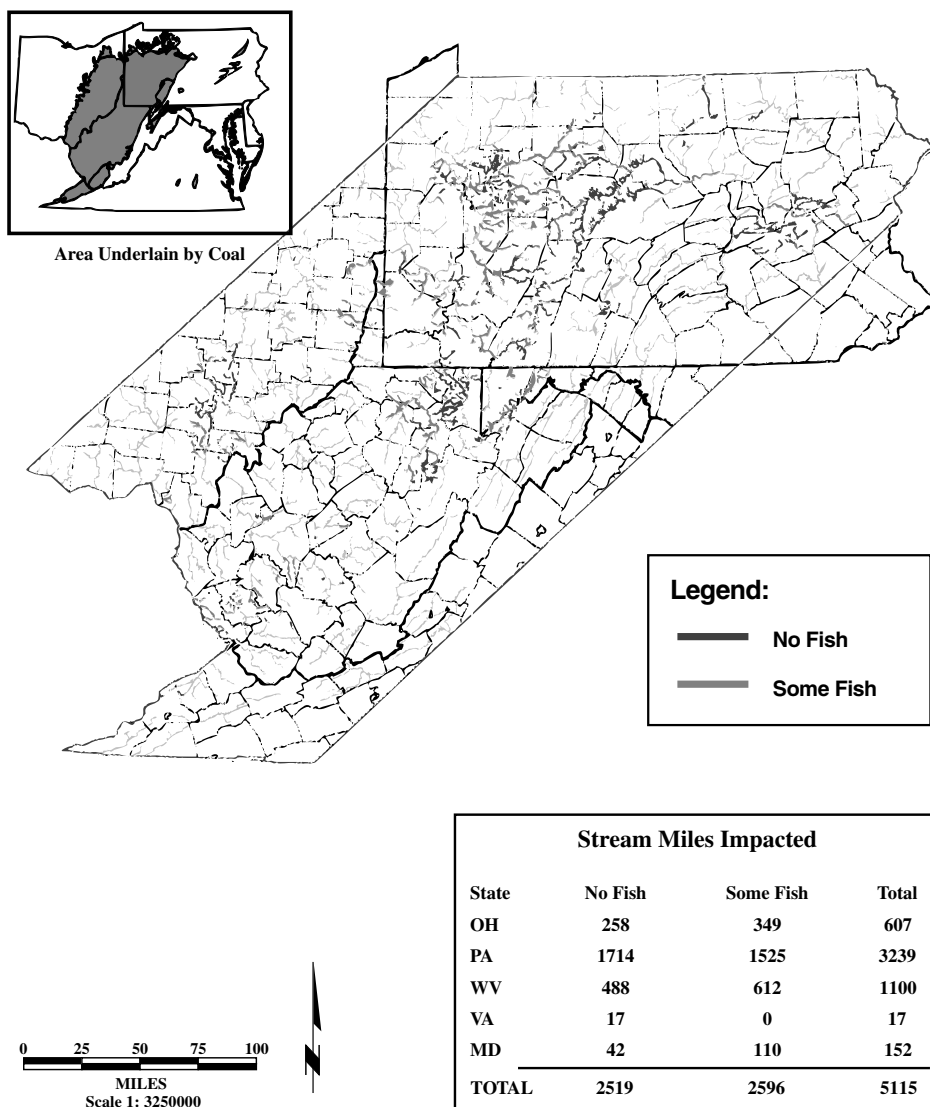


Figure 7.12 (Color figure follows p. 242.) Fish habitats affected by AMD within Maryland, Ohio, Pennsylvania, Virginia, and West Virginia. (From U.S. EPA, 1995.)

to devalue the dollar during future years of the treatment period. The annualized cost was obtained by converting the total system cost (NPV) to an equivalent annual cost so that each system could be compared equally on an annual basis. The information presented in Table 7.10 suggests soda ash has the highest labor requirements (10 h/week) because the dispensers must be filled by hand and inspected frequently.

Table 7.10 Costs in 1996 of Five Chemicals to Treat AMD in West Virginia

Chemical	Flow and Acidity Conditions			
	189 ^a	3780 ^a	945 ^a	3780 ^a
	100 ^b	100 ^b	500 ^b	2500 ^b
Soda ash				
Reagent costs	\$3,731	\$44,000	\$58,300	\$1,166,000
Repair costs	0	0	0	0
Annual labor	14,040	14,040	14,040	14,040
Installation costs	229	229	229	229
Salvage value	0	0	0	0
Net present value	75,052	244,679	245,774	4,911,804
Annualized cost	\$17,817	\$58,086	\$58,346	\$1,166,046
Ammonia				
Reagent costs	\$2,543	\$22,440	\$28,050	\$561,000
Repair costs	495	495	495	495
Tank rental	480	1,200	1,200	1,200
Annual labor	7,020	7,020	7,020	7,020
Electricity	600	600	600	600
Installation costs	1,936	6,357	6,357	6,357
Salvage value	0	0	0	0
Net present value	48,547	139,117	162,749	2,407,725
Annualized cost	\$11,525	\$33,026	\$38,636	\$571,586
Caustic soda (20% liquid)				
Reagent costs	\$5,174	\$79,341	\$99,176	\$1,983,520
Repair costs	0	0	0	0
Annual labor	7,020	7,020	7,020	7,020
Installation costs	283	5,478	5,478	5,478
Salvage value	0	0	0	0
Net present value	51,601	368,398	451,950	8,389,433
Annualized cost	\$12,250	\$87,457	\$107,292	\$1,991,636
Pebble quicklime				
Reagent costs	\$1,478	\$9,856	\$12,320	\$246,400
Repair costs	500	2,500	2,500	10,000
Annual labor	6,500	11,200	11,200	11,200
Electricity	0	0	0	0
Installation costs	16,000	80,000	80,000	120,000
Salvage value	0	5,000	5,000	20,000
Net present value	49,192	162,412	172,790	1,127,220
Annualized cost	\$11,678	\$38,556	\$41,020	\$267,600
Hydrated lime				
Reagent costs	\$814	\$9,768	\$12,210	\$244,200
Repair costs	1,000	3,100	3,500	10,500
Annual labor	6,500	11,232	11,232	11,232
Electricity	3,500	11,000	11,000	11,000
Installation costs	58,400	102,000	106,000	200,000
Salvage value	5,750	6,500	7,500	25,000
Net present value	94,120	228,310	242,809	1,313,970
Annualized cost	\$22,344	\$54,200	\$57,642	\$311,932

Note: Prices for the reagents, equipment, and labor are based on actual costs to mining operators in West Virginia. The analysis is based on a 5-year operation period and includes chemical reagent costs, installation and maintenance of equipment, and annual operating costs.

^a Flow, L/min.

^b Acidity, mg/L as CaCO₃.

Caustic soda has the highest reagent cost per unit or moles of acid-neutralizing capacity and soda ash has the second highest; however, soda ash is much less efficient in treating water than caustic soda. Hydrated lime treatment systems have the highest installation costs of the five technologies because of the need to construct a lime treatment plant and the need to install a pond aerator, although the cost of hydrated lime is low.

For a 5-year treatment period, ammonia had the lowest annualized costs for the low-flow/low-acid situation. Pebble quicklime is similar to ammonia in cost, and caustic is third. Soda ash is fourth because of its high labor and reagent costs, and hydrated lime is last because of its high installation costs. With the intermediate flow and acid cases, ammonia is the most cost-effective, with pebble

quicklime second. Hydrated lime and soda ash were next. Caustic soda is the most expensive alternative with these intermediate conditions. In the highest flow/acidity category, pebble quicklime and hydrated lime are clearly the least costly treatment systems, with an annualized cost \$260,000 less than ammonia, the next best alternative. The use of soda ash and caustic soda is prohibitively expensive at high flow and high acidity.

— Based on information supplied by J. G. Skousen, West Virginia University

PROBLEMS

- 7.1 Describe the potential environmental S impacts that could be expected to be associated with (a) an industrial region with factories that produce gaseous and solution S waste products that require disposal; (b) surface-mining operations that stockpile overburden materials, high in reduced-S minerals, close to a river; and (c) excessive S fertilization of coarse-textured soils that are overirrigated for the production of forages used for nonruminant animal feed.
- 7.2 Describe how animal toxicities occur when different types of S-containing feed supplements are used.
- 7.3 A coal-fired power plant must produce 250,000 MJ/h to supply enough steam to operate its electric generators to meet customer needs. How much coal would be required if the power plant used coal from the Northern Appalachian Region, San Juan River Region, or the Powder River Region? What additional operational concerns (e.g., price, quality, location) should be considered?
- 7.4 Calculate the difference in the quality (mol H⁺/L) of rainwater in an unpolluted area with a precipitation pH of 6.8 vs. an industrial region with a precipitation pH of 4.3.
- 7.5 What are the MRTs for S transfer through the biosphere, pedosphere, freshwater lakes, and oceans and seas?
- 7.6 What percentage of S released into the atmosphere is related to industrial processing sources (see Table 7.2 and Figure 7.3)?
- 7.7 What forms of S are present in soils? Which S forms are (a) the most important for plant nutrition; (b) dominant in surface horizons; and (c) found in subsoils of arid climates?
- 7.8 Why are S mineralization–immobilization processes important and what influence does the C:S ratio have on organic N and P mineralization and immobilization?
- 7.9 Why do plants require S? Describe the symptoms of plant S deficiencies. Discuss how plant S analysis can be used to determine if supplemental S might be needed for optimum plant growth (see Table 7.8).
- 7.10 A soil test indicates that 4.5 mg SO₄-S/kg is potentially available in a field that will be planted in alfalfa. This crop requires 22 kg S/ha for adequate yields. What amount of fertilizer S should be recommended?
- 7.11 Design a holistic S management program that includes irrigation, manure, fertilizers, and crop requirements. What other information would be needed in developing the management program?
- 7.12 Describe some of the problems that occur when hydric (wet) soils that contain reduced S are drained. Explain what type of reactions would be expected to occur as a hydric soil is drained and comes in contact with oxygen.
- 7.13 A bentonite (Na-saturated 2:1 clay) mine land contains an area with sodic soils that have an ESP of 40% and a CEC of 30 cmol/kg. Determine the GR for lowering the ESP to 5%. If a local source of gypsum is available, how much of this material should be applied to a 10-ha area on the bentonite mine site?
- 7.14 Use of soil amendments has been advocated where high sodic CBM waters are land-applied. These waters are dominated by NaHCO₃ with SARs as high as 70. Explain what amendments or cultural practices could be used to ameliorate the potential problems that might occur with the land application of CBM waters.
- 7.15 Calculate the difference in cost per liter for treating acid mine drainage that has a flow of 3780 L/min and acidities of 100 or 2500 mg/L using the information in Table 7.10. Determine the difference for each of the reagents — soda ash, ammonia, caustic soda, pebble quicklime, and hydrated lime — using the 1996 data.

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Nutrient Management Planning

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8.1 NUTRIENT MANAGEMENT PLANNING: BASIC PRINCIPLES

Nutrient management plans (NMPs) begin with an understanding of all factors controlling the flux of nutrients into and out of any ecosystem. For agriculture, nutrients enter farms as production inputs (feed, forage, bedding, livestock, fertilizer, biosolids, i.e., sewage sludges, manures, N fixed by legumes, atmospheric deposition). Some nutrient inputs leave farms in agricultural products (meat, milk, eggs, grain, hay, straw, silage, manures). And, because agricultural systems are not 100% efficient, some nutrients remain on farms, accumulating in soils, animals, and perennial crops, or are lost from farms by erosion, runoff, leaching, volatilization, and denitrification. Well-designed NMPs seek to minimize nutrient losses, which are unprofitable and often damaging to air, soil, and water quality.

Historically, nutrient management planning has been a voluntary activity, mainly conducted for agriculture, by farmers, based on advice from specialists at universities, state or federal advisory agencies, or private consultants. However, the past decade has seen the emergence, worldwide, of laws and regulations that now mandate NMPs in some settings, primarily because of increasing

evidence for the impact of agricultural nutrients on water quality. In the United States, the advent of a regulatory approach for NMPs has primarily been driven by the need to improve nutrient management by animal-based agriculture (see Environmental Quality Issues/Events Box, Nutrient Management Legislation and Policies in the United States: Voluntary or Regulatory?). Similar changes have occurred in Europe; readers are referred to Nutrient Management Legislation in European Countries (De Clercq and Sinabell, 2002) for details on the evolution of environmental policies related to nutrient management in 15 of the member states of the European Union (EU).

Although production agriculture has long been the main arena where voluntary, and now mandatory, NMPs have been developed and implemented, emerging concerns about the impacts of all sources of nonpoint nutrient pollution have recently resulted in application of the NMP concept to other land uses. For example, some states now require large-scale urban horticultural operations (e.g., golf courses, commercial landscapers), and municipalities (city parks and recreational areas) relying upon land application to recycle biosolids and composts to develop NMPs using the same principles as production agriculture. Regardless of the land use, it is vital to implement NMPs that address production, profitability, and environmental quality in a holistic manner. The increasingly global nature of nutrient cycling and transfer from land to water and air also demands that we develop NMPs that function at larger geographic scales, such as watersheds and ecoregions, and across national and international political boundaries.

8.1.1 Definition and General Goals of Nutrient Management Plans

An NMP is defined as a detailed, site-specific plan for a farm (or any enterprise managing nutrients) that recommends an approach for providing plants with the nutrients needed to achieve economically optimum yields while minimizing the negative impact of nutrients on the environment. The foundation of any NMP is the concept of nutrient mass balance. Simply stated, in a well-designed NMP, nutrient inputs to the system being managed should be balanced, as closely as possible, by nutrient outputs. If a nutrient deficit exists, soil fertility will gradually decline, leading to plant nutrient deficiencies and reductions in crop yields or plant performance. Nutrient surpluses can also occur and are a common occurrence on livestock farms, as illustrated by several examples from the EU (Table 8.1) and a recent county-by-county survey of manure P surpluses in the United States (Figure 8.1). Excess nutrients present on farms, or at larger geographic scales (watersheds, counties), either accumulate in soils or are lost to surface waters or groundwaters, or the atmosphere, often with undesirable environmental impacts (Figure 8.2). Properly structured, efficient NMPs integrate nutrient balance into all management decisions, use site-specific best management practices (BMPs) to prevent nutrient losses, and include monitoring strategies to document the success, or failure, of each component of the plan. Modern NMPs consider three key dimensions of this complex, vitally important planning process (Beegle et al., 2002):

1. *Strategic*: This is the highest level of planning and focuses on long-term goals and strategies to achieve these goals. Much of the information needed for strategic NMPs and many constraints to accomplishing defined goals originate outside an operation. Strategic management begins with determination of broad, long-term goals, followed by a critical assessment of the current situation, including strengths and weaknesses, an evaluation of resources available (or lacking) to meet goals, and results in the most efficient allocation of resources needed to achieve long-term objectives. Strategic planning addresses the financial, personal, sociopolitical, and legal aspects of an operation and establishes performance criteria to judge long-term success.
2. *Tactical*: The tactical level of an NMP focuses on implementing strategic goals and operates on a timeframe of a few months to a few years. Tactical planning focuses on implementation of the many decisions about an operation that were already made in accordance with strategic goals (e.g., the amount of land available, number of animals in the operation, crop rotations, availability of equipment and labor, need for more permanent soil/water conservation BMPs). It is critical to recognize that tactical management cannot be successful in the long run unless it operates within clearly defined strategic goals.

Table 8.1 Farm-Gate Nutrient Budgets for Various Types of Animal Operations in the European Union

Item	Dairy						Pig											
	Belgium ^a			Sweden ^b			UK ^c			Belgium ^d			Denmark ^e			France ^f		
	N	P		N	P		N			N	P		N	P		N	P	
Input	— kg ha ⁻¹ —																	
Mineral fertilizer	228	13		65	1		244			0	0		60	1		44		9
Manure	0	0		0	0		0			0	0		0	0		0		0
Fodder	67	10		80	17		0			0	0		438	95		0		0
Concentrates	162	31		0	0		51	27		32060	5859		0	0		542		95
Animal products	17	5		0	0		0	0		2970	561		0	0		2		0.4
Atmospheric deposition	40	1		4	0		40	0.2		0	0		28	0		22		0
Symbiotic fixation	0	0		29	0		10	0		0	0		0	0		0		0
Total Input	514	60		178	18		345	43		35030	6420		526	96		610		104
Output																		
Organic fertilizers	71	12		0	0		0	0		11960	2945		0	0		116		41
Arable products	7	2		4	1		0	0		0	0		99	16		0		0
Animals and animal products	105	23		48	9		65	17		12951	2355		147	30		191		49
Other	0.9	0.2		0	0		0	0		308	64		0	0		0		0
Total Output	184	37		52	10		65	17		25219	5364		246	46		307		90
Surplus	330	23		126	8		280	26		9811	1056		280	50		303		14
Utilization (%)	36	62		29	56		19	39		72	84		47	48		50		86

^a Farm with 26 ha of grassland, no arable crops, and 39 dairy cows.

^b Farm with 48 ha of arable cropland, 41 dairy cows, 15 heifers, and 40–60 beef cattle.

^c Farm with 76 ha of grassland, 102 dairy cows, and 70 replacement heifers.

^d Farm with no agricultural land and 2000 pigs, with 2.5 production cycles per year.

^e Average of 13 pig farms, averaging 79 ha of fallow and grassland (14%), cereal and other crops (86%), and 216–387 sows.

^f Farm with 50 ha of arable crops and 220 sows.

Source: De Clercq, P. et al., *Nutrient Management Legislation in European Countries*, Wageningen Pers, Wageningen, the Netherlands, 2002. With permission.

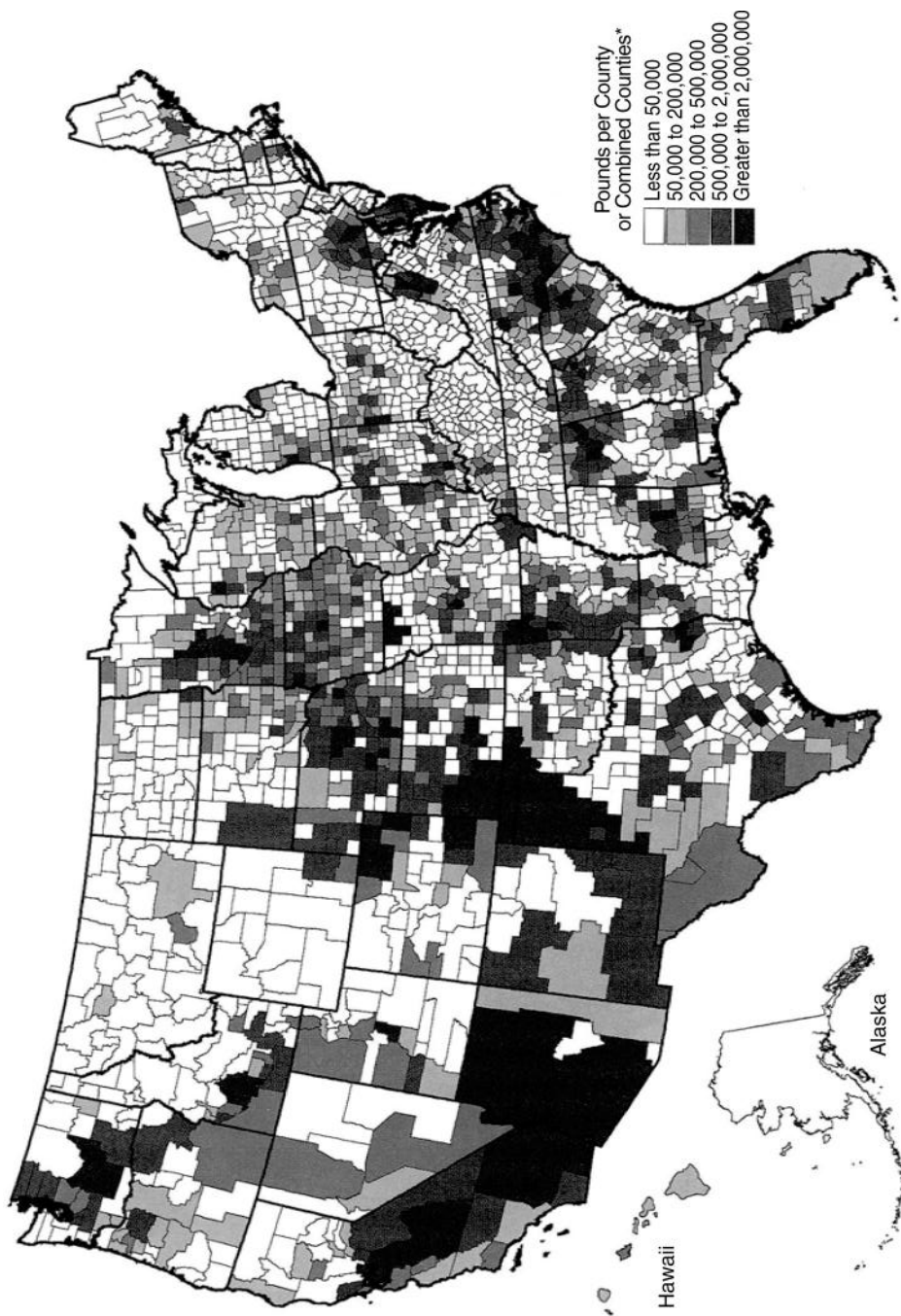


Figure 8.1 Analysis of the availability of animal manure P, relative to crop P needs, in the United States. County nutrient balances assume no manure export from farms.
(From Kellogg et al., 2000.)

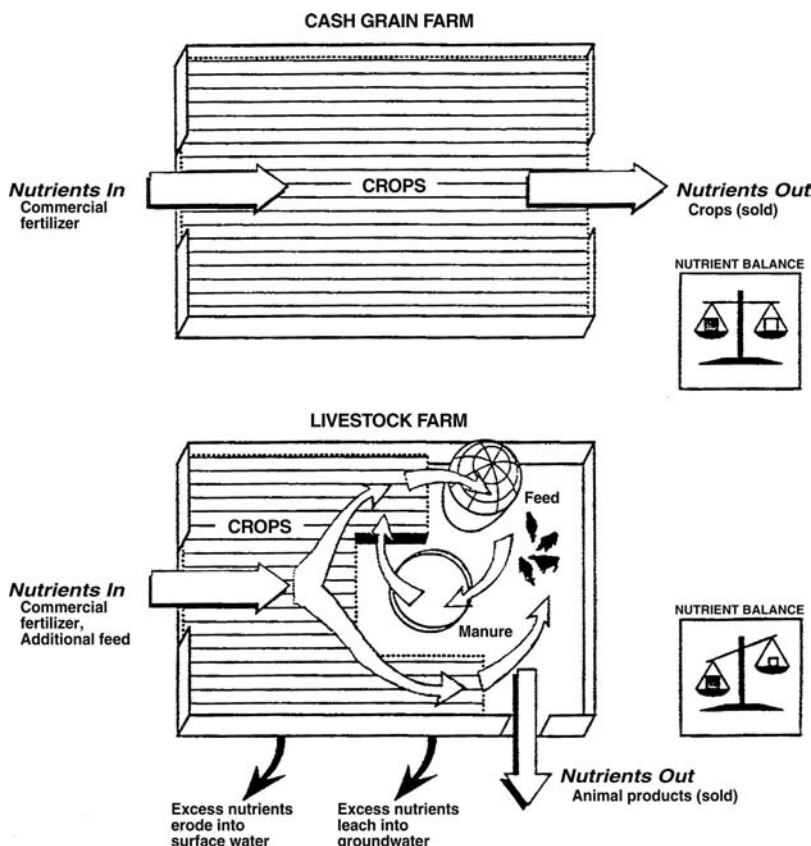


Figure 8.2 Comparison of nutrient balances for cash grain and livestock farms, illustrating the more complex nature of nutrient cycles for livestock operations. (Adapted from Weidner, K., *Pa. State Agric.*, Spring/Summer, 2, 19, 1988.)

3. *Operational:* The operational dimension of an NMP addresses the immediate needs and actions to implement the tactical plan and is short term in nature (days to weeks). At the operational level, the focus is on weather, soil conditions, scheduling of labor and equipment, interactions with suppliers, and similar practical factors. As with tactical planning, operational decisions must reflect strategic goals if NMPs are to be successful. It is important to recognize, however, that uncontrollable factors that arise during the operational phase (e.g., bad or extreme weather events, equipment malfunctions, or financial emergencies) can result in problems or delays that prevent the effective implementation of well-designed strategic and tactical plans.

In summary, the broad design and essential practical components of agricultural NMPs are well established and institutionalized in many countries in documents such as the U.K. “Codes of Good Agricultural Practice” and the USDA-NRCS Code 590 Nutrient Management Standard.* We describe the basic components integral to all NMPs in this chapter using agricultural settings, such as farms with and without animal production operations, because they represent the sectors where the NMP concept has been most widely applied. Factors to consider when developing NMPs for other situations, such as urban horticulture, land reclamation, and the land application of municipal biosolids, a process regulated by state and federal laws, are briefly described to illustrate some additional aspects of NMPs. Following a general overview, detailed examples of site-specific

* See <http://www.nrcs.usda.gov/technical/ecs/nutrient/590.html> for the NRCS Code 590 standard.

management practices used in agriculture, but important to all who develop NMPs, are provided for the two nutrients that have the most significant environmental impacts, nitrogen (N) and phosphorus (P).

8.1.2 Basic Components of Agricultural Nutrient Management Plans

Nutrient management on any farm begins with a quantitative assessment of the current balance between nutrient inputs to the farm and nutrient outputs from the farm, referred to as a nutrient budget. In essence, we seek to determine if farming practices are “overloading” some transformation in a biogeochemical cycle resulting in a negative effect on an adjacent ecosystem. Practically speaking, in most agricultural situations, only a limited number of biogeochemical cycles are actually “managed” by farmers or those involved in advising farmers. Agricultural research has shown that the most important and readily manipulated nutrient cycles from a crop production standpoint are N, P, and potassium (K). The carbon (C) cycle must also be considered because of its role in the mineralization or immobilization of N and P. Historically, farmers have not actively managed the cycling of C in soils other than through general efforts to maintain or build soil organic matter. This may change in the future, given recent interest in the potential to use C sequestration by soils as a component of the global effort to address climate change problems, primarily emissions of CO₂ from burning fossil fuels. Carbon sequestration has been defined as the storage of C in a stable solid form, through direct and indirect fixation of atmospheric CO₂, such as by photosynthesis and subsequent return of plant biomass to soils (SSSA, 2001). The top meter of soil contains about 75% of the Earth’s terrestrial C and has the potential to sequester additional C through improved management of crop-, grazing, and forestlands. Many U.S. soils have lost as much as 50% of their original C content due to the effects of land clearing and tillage management. Practices, such as conservation tillage and the use of improved crop cultivars, can prevent further C loss and even promote accumulation of stable soil C. Interest is growing in the possible economic value of soil C as an agricultural commodity, both to offset C losses from fossil fuel use, and to restore degraded soils.

Proper management of soil pH through liming is also important to NMPs and usually ensures that the calcium (Ca) and magnesium (Mg) cycles provide adequate amounts of these nutrients for plant growth without toxic effects from the acidic cations hydrogen (H), aluminum (Al), and manganese (Mn). Sulfur (S) and trace element cycles are normally of less concern for crop management except in certain well-understood, localized conditions. As an example, S deficiency and significant crop responses to applications of S fertilizers are most common in humid regions on deep, sandy soils (see Chapter 7); trace element deficiencies are usually restricted to alkaline or overlimed soils, i.e., iron (Fe), Mn, zinc (Zn), or high organic matter soils, i.e., copper (Cu) (see Chapter 9).

Nutrient budgets have traditionally been constructed first at the field level, then for the whole farm by combining budgets from all fields. The first step in this approach is to estimate crop nutrient requirements using realistic yield goals. Realistic yields are defined as expected crop yields that can realistically be achieved given the limits established by soil productivity, crop genetics, climate, management skill and intensity, economics, and the need to protect and improve environmental quality. Several methods to determine realistic crop yields are available. The most accurate is to keep long-term yield records and use some form of “rolling average.” In this approach the latest yield data for a field for a specified time period (e.g., the last 7 years) are used. Each year, the oldest yield data are dropped from the database, the newest yield data are added, and an updated realistic yield goal is determined. Farmers can also estimate realistic yield goals from crop variety trials conducted by universities and industry or base them on state or country averages for different soil productivity classes. Next, contributions of soil nutrients are assessed by a comprehensive soil testing program, one that may even include subsoil testing for some nutrients found below the “plow layer,” but within the rooting zone of the crop. Sulfur is a good example of a nutrient where

subsoil testing is important. Many studies have shown that the sulfate form of S (SO_4^{2-}) leaches to only moderate depths in soils and that subsoil S can be an important reservoir of plant-available S once roots penetrate to subsoil horizons. Subsoil testing for soil nitrate-N ($\text{NO}_3\text{-N}$) can also be effective in areas with low rainfall. Late fall or spring deep soil tests (e.g., 1 to 1.5 m) for $\text{NO}_3\text{-N}$ can identify the amount of N that may be available to this year's crop from the past year's fertilizer or manure applications. Soil test estimates of the amount of plant-available soil nutrients are used to determine the probability of an economic crop response to nutrient applications and help us to quantify the nutrient application rates needed for optimum crop yields. Nutrients available from irrigation waters and biological N fixation should also be considered in the nutrient budget. The difference, for all farm fields, between crop nutrient requirements and nutrients available from soils, irrigation waters, and N fixation, is the amount of available nutrients needed from on-farm and off-farm sources to attain desired crop yields.

If nutrient budget calculations indicate a nutrient deficit exists, efficient and economical use of off-farm nutrients becomes the key goal of the NMP. This most commonly occurs with farms that do not have a significant animal production component. For such farms, the focus is on the economics of purchasing commercial fertilizers, or perhaps importing manures or biosolids, and then applying them to cropland in an efficient manner. However, if a farm has a nutrient surplus, as is often the case for farms with large animal numbers, the NMP must account for the amount, plant availability, storage, and land application of nutrients present on the farm in animal by-products (manures, composts, lagoon wastewaters). Most states provide reasonable estimates of the total nutrient content of animal manures so that farmers can adjust fertilizer applications by proper crediting of manure nutrients (Table 8.2). Methods to estimate plant availability of manure N are well developed because N is often used as the criterion to determine manure application rates (see Section 5.2.5). Less information is available on plant availability of other elements in manures. If manure nutrient surpluses are consistently present, plant nutrients, and some potentially harmful trace elements found in manures, e.g., arsenic (As), Cu, selenium (Se), Zn, may build up in soils, especially those in close proximity to the site of manure generation. If these elements accumulate in soils to the point that they can have a significant impact on the environment, the NMP must also include strategies to minimize that impact. Note that the buildup of nutrients to "excessive" levels in soils is not confined to animal-based agriculture. Other examples are vegetable farms with high soil nutrient levels from long-term overapplication of commercial fertilizers and farms operated by municipalities or industries specifically to dispose/recycle organic or inorganic by-products.

A second, broader approach to construction of nutrient budgets is the use of "farm-gate" balances. In this method, farmers simply calculate total farm inputs and outputs to determine if a nutrient surplus or deficit exists, as shown in Table 8.1. The magnitude of the surplus or deficit then guides strategic planning efforts. In the Netherlands, this approach is now used as the primary

Table 8.2 Average Concentrations (% on a dry weight basis) of N, P, and K in Animal Manures

Animal Type	N	P	K
Beef	3.25	0.96	2.08
Dairy	3.96	0.67	3.16
Poultry (layers)	4.90	2.08	2.08
Poultry (broilers)	4.00	1.69	1.90
Sheep	4.44	1.03	3.05
Swine	7.62	1.76	2.62
Turkey	5.96	1.65	1.94

Source: Sharpley et al., 1998. With permission.

criteria to identify the risk of nutrient loss from a farm. Neeteson et al. (2001) reviewed the Dutch approach and stated, “from the mid-nineties, policy-makers, environmentalists, and farmers organizations agreed that the pollution risks are determined by the differences between inputs from outputs, i.e., by the farm surplus, rather than by the input of manure only. Therefore, a mineral accounting system (MINAS) was developed.” Today, Dutch farms with more than 2 LU/ha (livestock units per hectare) must participate in the MINAS program, which involves the calculation, estimation, and reporting of major inputs and outputs to the farm. Farms that exceed a permitted N or P surplus must pay a “levy” (fee) to the agency responsible for the MINAS program. In 2001, the levy was ~\$3.10/kg of P and \$1.10/kg of N. In 2003, the “levy-free” surplus for arable cropland will range from ~56 to 100 kg N/ha, depending on soil type, and ~9 kg P/ha. It is believed that the fees will provide economic incentives that foster innovative strategies and eventually result in “nutrient-balanced” farms, which, in turn, will have lower risks of N and P losses to the environment.

Actual implementation of an NMP based on a farm nutrient budget requires consideration of specific BMPs that address the amount, form, storage, placement, and timing of application of nutrient sources (fertilizers, manures, biosolids, composts) relative to the type of plants grown and characteristics of the land where nutrients will be applied. More detailed, comprehensive NMPs (CNMPs) are needed for agricultural operations that produce animals or animal products, referred to as “animal feeding operations” (AFOs) or “concentrated animal feeding operations” (CAFOs). The six basic components of a CNMP were defined by USDA-NRCS in 2000: “CNMPs will contain actions that address soil erosion and water quality criteria for the feedlot, production area, and land on which manure and organic by-products will be applied.” These components are (1) manure and wastewater handling and storage; (2) land treatment practices; (3) nutrient management; (4) record keeping; (5) feed management; (6) alternative uses for manures.* The basic components of an agricultural NMP/CNMP are given in Table 8.3.

Table 8.3 Overview of the Major Components of a Comprehensive Nutrient Management Plan

Component	Specific Information and Action Required
Farm identification and natural resource inventory	Operator's and owner's name, address and phone number, location and boundaries of all cropland owned and rented, individual field boundaries, field numbers and size, hectares of each crop type and “realistic yield goals,” total amount of land where manure will be applied, animal types and number of animal equivalent units (AEUs) per hectare, soil types and slopes, areas where manure application should be limited, receiving waters and their designated uses, intakes to agricultural drainage systems, drinking water wells and springs, special protection groundwaters and surface waters, and areas of concentrated flow, such as ditches, grassed waterways, gullies, and swales
Soil testing	Routine agronomic soil tests usually include pH, lime requirement, organic matter, and plant-available P, K, Ca, and Mg; other special tests, such as the PSNT, S, trace elements (boron, Cu, Fe, Mn, Zn) soluble salts, texture, cation exchange capacity, P saturation, and P sorption capacity, may be useful in some cases; soil samples should represent each field or management unit and each soil type; in general, soil tests (except the PSNT which is done each year) should be repeated every 2 to 3 years, at the same time of year, and records should be kept to monitor changes in soil fertility due to variations in soil and crop management on the farm.
Plant analysis	Plant tissue tests can help to diagnose nutrient deficiencies and are useful tools to determine if nutrient management practices need to be changed either during this growing season or for the next crop; two important new approaches to N testing for corn (and some other crops) that should be used each year are the LCM and the corn stalk nitrate test, which can provide both information on the need for N fertilization this year (LCM) and the success of an N fertilization program at the end of the year (corn stalk nitrate test)

continued

* See <http://www.nrcs.usda.gov/programs/afo/> for information on USDA-NRCS CNMPs.

Table 8.3 Overview of the Major Components of a Comprehensive Nutrient Management Plan (continued)

Component	Specific Information and Action Required
Organic by-product analysis	Animal wastes should be tested, at a minimum, for total N, ammonium-N, and total P and K; samples should be taken as close to the time of application as possible; if other organic wastes are land applied (e.g., municipal biosolids), they should (or must) be tested for nutrients and specific pollutants required by state and federal environmental agencies
Feed and crop management	In general, animal-to-land ratios that result in the efficient recycling of nutrients in manures on the farm and achieving nutrient mass balance; animal diets can be modified to reduce nutrient concentrations in manures (for example, diets including low-phytate corn and phytase enzymes can reduce P excretions by poultry and swine); the result is a manure with a N:P ratio that more closely matches that required by crops; crop rotation and cultural practices should also be implemented that maximize economic feed production and nutrient recycling
Nutrient application practices	Best management practices for nutrient applications are based upon “realistic crop yield” goals, cropping history, and results of soil, plant, and organic waste tests; once the most efficient nutrient application rates are identified, select the most economic nutrient sources that meet crop needs and minimize losses to the environment; carefully assess nutrient application methods, timing, and placement, plant nutrient uptake patterns, and pathways of nutrient loss
Animal manure storage and barnyard management	All wastes and by-products (manures, composts, dead animals) should be handled and stored in a manner that does not adversely affect groundwater or surface water or create public health concerns; clean water should be diverted from contact with organic wastes, adequate storage capacity should be provided, runoff into surface waters and contaminant migration to groundwaters should be prevented, losses of nutrients to the atmosphere should be minimized, and treatment should be carried out to reduce odors, pathogens, and the attraction of vectors
Soil and water conservation practices	Conservation practices should be implemented that minimize the movement of soil, organic materials, nutrients, and pathogens from lands where fertilizers and organic wastes have been applied; measures that help to achieve these goals include riparian buffers, filter strips, vegetated field borders, grassed waterways, contour buffer strips, conservation tillage, rotational grazing and pasture management, and grassed waterways
Alternative uses for surplus nutrients	In areas where animal manure production and nutrient content exceed crop nutrient needs, plans for utilizing surplus nutrients (manure excesses) are needed; some options include selling manure to farmers with a sufficient land base to use the manure nutrients, composting manures for use by home owners, or incinerating the manure for use in power generation; the chosen options should not be detrimental to the environment or public health, and must comply with existing laws that govern alternative uses; the plan should include information on the amount of manure which will be exported, the name and location of the importing operation, the nutrient content of the manure, and the planned use of the manure, including anticipated application rates
Monitoring and record-keeping	Accurate records and regular monitoring are needed to determine how well a CNMP is working; records should be kept of soil testing results, analyses of manure and other nutrient sources, and plant tissue testing, as well as records on crop yields, manure production, manure exports, nutrient application rates, and timing, location, and methods of application; these records will help show if nutrients are being managed in a manner that prevents losses to the environment while sustaining “realistic yields”; all nutrient management plans should be reviewed annually, and as part of the review process, significant changes in management or unforeseen circumstances that require a modification of the plan should be addressed (i.e., increases in the AEUs/ha, major decline in crop yields, animal disease outbreak, development of new BMPs, unforeseen severe weather conditions)

Example Problem 8.1

The Belgian dairy farm in Table 8.1 determines that by feeding closer to the cows' nutritional requirements it can reduce the amount of N and P imported in concentrates by 30%. By improving crop N management, the farm can also reduce mineral N fertilizer use by 25%. How do these changes affect the N and P surplus and utilization percentages on this farm?

Current total N and P inputs to farm = 514 kg N/ha and 60 kg P/ha

Current total N and P outputs from farm = 184 kg N/ha and 37 kg P/ha

Inputs of N and P as feed concentrates = 162 kg N/ha and 31 kg P/ha

Inputs as feed concentrates with 30% reduction in dietary N and P = 113 kg N/ha and 22 kg P/ha

Reduction in N and P imports in feed concentrates = 49 kg N/ha and 9 kg P/ha

Inputs of N in mineral fertilizers with 25% reduction = 171 kg N/ha

Reduction in mineral N fertilizer inputs = 57 kg N/ha

New total N inputs to farm = $(514 \text{ kg N/ha}) - (49 \text{ kg N/ha} + 57 \text{ kg N/ha}) = 408 \text{ kg N/ha}$

New N surplus = $(408 \text{ kg N/ha} - 184 \text{ kg N/ha}) = 224 \text{ kg N/ha}$

New % utilization of N = $(184 \text{ kg N/ha}) / (408 \text{ kg N/ha}) = 0.45 = 45\%$

New total P inputs to farm = $(60 \text{ kg P/ha} - 9 \text{ kg P/ha}) = 51 \text{ kg P/ha}$

New P surplus = $(51 \text{ kg P/ha} - 37 \text{ kg P/ha}) = 14 \text{ kg P/ha}$

New % utilization of P = $(37 \text{ kg P/ha}) / (51 \text{ kg P/ha}) = 0.73 = 73\%$

Spatial aspects of NMP implementation are also important to farm profitability and environmental quality. The *site plan* in Figure 8.3 was developed for a dairy farm and shows factors to be considered if we are to ensure that one ecosystem (the farm) does not adversely affect an adjacent ecosystem (riparian zone, stream). It is an integrated CNMP that addresses all steps needed to store, handle, and distribute nutrient from manures and fertilizers to a variety of crops. Environmental protection practices include storm-water runoff ponds, riparian corridors, and proper placement of animal and manure production facilities relative to drinking water wells.

8.1.3 Nutrient Management Plans for Other Land Uses

As mentioned above, other land uses beyond production agriculture may require development and implementation of NMPs. For example, the state nutrient management law in Delaware requires that NMPs be developed for anyone who manages more than 4 ha of land on which nutrients are applied or operates an animal operation in excess of eight animal units.* Today, NMPs are being implemented by golf courses, commercial landscapers, production nurseries and greenhouses, small horse farms, and many small farms where poultry are raised but crops are not grown. The NMPs follow similar criteria as agricultural plans, but are modified to meet the specific characteristics of different land uses, as shown in Table 8.4 for golf courses.

* See <http://www.state.de.us/deptagri/nutrients/index.htm> for details on the DE NMP program.

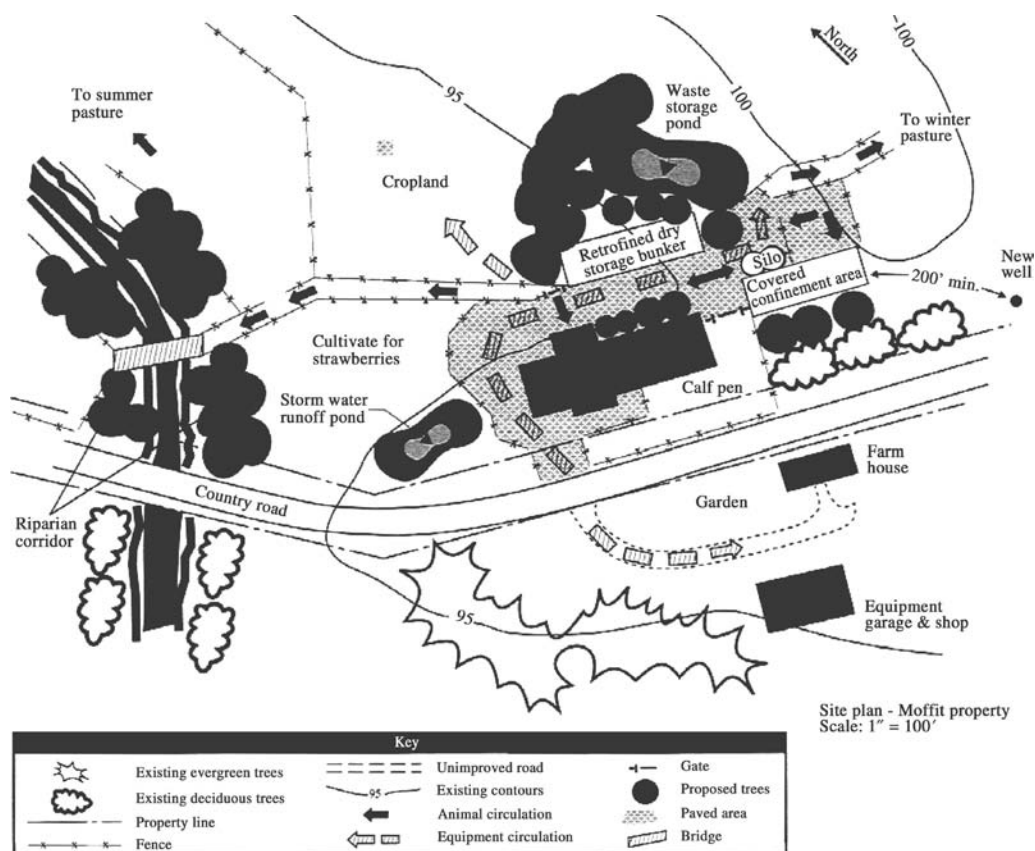


Figure 8.3 Site plan developed for an animal manure management system. (From U.S. Department of Agriculture, Soil Conservation Service, 1992.)

Table 8.4 Recommended Elements in a Nutrient Management Plan (NMP) for Golf Courses

Element	Information Needed for Nutrient Management Plan
Plan identification	Operator information (name, address, phone number), watershed identifier, nutrient consultant information, overview of characteristics of operation
Site description	Field maps, aerial photographs of golf course layout, indicating types and location of turf grass; soil survey maps of all soil types indicating soil texture; location of all surface waters including drainage ditches, streams, and ponds
Turf grass and nutrient management practices	Total area of land represented by the NMP; soil sample analyses (not older than 3 years); summary of recommended nutrient application rates; description of irrigation systems (well, pond, recycled water) and methods and timings used to apply fertilizers and other nutrient sources; current and planned turf grass species; turf establishment and age; mowing management (height, times per year); turf clipping management (removal or recycling of clippings)
Best management practices	Description of BMPs needed or already implemented to prevent nutrient loss to water (e.g., buffer strips, grassed waterways, wetlands, practices for control of point sources such as fertilizer mixing areas)
Record keeping and reporting	Maintain records and submit annual reports providing: soil test results and recommended nutrient application rates; amount of organic and inorganic fertilizers applied and the quantity of land to which applied; dates and methods of nutrient application; any changes in the nature of the operation (e.g., > 25% increase in turf grass area)

Source: Delaware Nutrient Management Commission, 2003.

Urban areas also produce large quantities of a wide variety of organic by-products that are suitable for land application. Examples include biosolids, composts of biosolids and wood by-products, solid by-product composts (with or without biosolids), yard waste (leaves, grass clippings) composts, and wastewaters from sewage or drinking water treatment plants. These materials are commonly applied to cropland, forests, turf and ornamentals grown in landscapes and roadsides, and in large-scale land reclamation projects, such as mine spoils. Land application of municipal by-products is almost always regulated by federal and state environmental agencies. Normally, permits must be obtained from these agencies following a review process that requires detailed and site-specific information on all aspects of the land application program including, but not limited to, soil type, crop rotation, groundwater and surface water properties, topography, odor control, and monitoring programs. Unlike agricultural situations where only a few biogeochemical cycles must be managed and monitored, environmental regulatory agencies require that management plans for municipal and industrial by-products carefully consider a large number of inorganic and organic constituents (Table 8.5).

Table 8.5 Monitoring Requirements for Municipal Biosolids in Delaware

Inorganic By-Product Constituents^a	Priority Pollutants^b
Total N	Volatile compounds
NH ₄ -N	Benzene
NO ₃ -N	Carbon tetrachloride
P	Chloroform
K	Toluene
Ca	Trichloroethylene
Mg	Vinyl chloride
Hg (mercury)	
Na (sodium)	Acid compounds
Cu	Pentachlorophenol
Ni (nickel)	Phenol
Zn	
Pb (lead)	Base/neutral compounds
Cd (cadmium)	Hexachlorobenzene
Cr (chromium)	Phenanthrene
CN (cyanide)	Pyrene
pH	
	Pesticides and PCBs
	Aldrin
	Chlordane
	2,4-D
	Dieldrin
	Heptachlor
	Toxaphene
	Polychlorinated biphenyls (PCBs)

^a Total analysis required.

^b Representative examples of each class given; in 1988, there were 126 priority pollutants identified by the EPA.

Source: Delaware Department of Natural Resources and Environmental Control, 1988.

Management and monitoring programs in NMPs for biosolids, therefore, must be based on our understanding of complex biogeochemical cycles for many elements or compounds. Regulatory agencies often use the *land limiting constituent* (LLC) concept to determine annual application rates and the total “site-life,” or length of time a by-product can be applied to a site. The LLC is the element or compound in a by-product perceived to present the greatest hazard and which should be used to determine the actual rate of by-product applied to a site this year and in total. Typical LLCs are nutrients, trace elements, and organic compounds (Table 8.6).

In 1992, the U.S. Environmental Protection Agency (EPA) released the “National Sewage Sludge Rule” as required by the U.S. Clean Water Act (40 CFR, Part 503). Commonly known as the Part 503 Rule, this document provides regulations developed in a comprehensive risk assessment of more than 15 years of research and management programs using biosolids for farms, gardens, forests, and at dedicated sites (e.g., landfills). It describes required management practices for biosolids use in land application programs. With respect to nutrients, the requirement is to apply biosolids at an “agronomic rate” that (1) provides the amount of N needed by the food, feed, and fiber crops, or other vegetation grown on the land; (2) minimizes the amount of biosolid N passing below the root zone of the crop or vegetation to groundwater. Agronomic rates are based on plant available N in biosolids, taking into account both inorganic N and the percentage of mineralizable organic N in these materials (see Section 5.2.5). Organic N mineralization rates vary among types of biosolids. Typical first-year percentages for organic N mineralized are 10% for composts, 20% for anaerobically digested biosolids, and 30% for aerobically digested and lime-stabilized biosolids. The agronomic rate can be based on crop P needs if it is determined that biosolid P use may pose a threat to surface water quality.

The Part 503 Rule also states that BMPs to control runoff (e.g., buffer zones) can be required and that landscapers or homeowners must be provided with instructions on the proper means to use products derived from biosolids (e.g., composts) for horticultural purposes. Careful record keeping, monitoring of biosolids for pollutant composition, and practices to ensure that threatened or endangered species are protected are also required under the Part 503 Rule.

Table 8.6 Example of the Approach to Determine the Land Limiting Constituent (LLC) for Land Application of Municipal Biosolids

Parameter	Quantity Generated (kg/yr)	Site Assimilative Capacity (kg/ha/yr)	Land Area Requirement (ha)
Total N	3000	400	8 [LLC]
P	2100	400	5
Ca	1.5	0.5	3
Cu	10	14	1
Ni	25	14	2
Pb	45	56	1
Zn	160	28	5

Assumptions:

1. Site-assimilative capacity for N based on crop uptake, ammonia volatilization, and requirement that nitrate loss in drainage waters will not exceed 10 mg NO₃-N/L.
2. Site-assimilative capacity for P recognizes the fact that, since biosolids are applied to meet crop N requirements, excess P (beyond crop requirements) will be applied. Conservation measures are thus required at the site to minimize P losses in runoff, erosion, and drainage.
3. Site-assimilative capacity for metals based on maximum cumulative metal-loading rate at the site, assuming a CEC of 10 cmol (+)/kg and a 20-year “site-life.” Under current Delaware regulations, these values are 10, 280, 280, 1120, and 560 kg/ha for Cd, Cu, Ni, Pb, and Zn. Using Cu as an example: site-assimilative capacity = 280 kg/ha ÷ 20 years = 14 kg/ha/year.
4. The LLC is defined as the constituent that requires the most land for safe utilization of the biosolids based on site-assimilative capacity. In this case the LLC will be N, which requires 8 ha.

Source: Delaware Department of Natural Resources and Environmental Control, 1988.

Environmental Quality Issues/Events

Nutrient Management Legislation and Policies in the United States: Voluntary or Regulatory?

Until the mid-1990s there were few national or state regulations in the United States that directly addressed nutrient management by agriculture. This gradually began to change due to growing national concerns about the potential water quality impacts of AFOs/CAFOs. The Clean Water Act (CWA) of 1972 (and amended in 1987) previously designated some CAFOs as point sources of pollution and required them to obtain NPDES permits to operate in a manner that prevented point-source discharge to surface waters. However, nonpoint pollution from land application of manures and wastewaters was not regulated, nor were poultry and pig CAFOs, and groundwater impacts were not covered at all by the CWA, which only addresses surface water quality. Many significant changes in environmental policy that affect nutrient management by CAFOs (federal policy) and AFOs (mainly state policies) have occurred since 1997. At the national level, the most significant changes were the development and now emerging implementation by EPA of the total maximum daily load (TMDL) program and the recently revised federal CAFO rule.

The CWA requires all states to develop TMDLs for pollutants of concern for surface water quality. A TMDL sets a limit on the amount of a pollutant that can be discharged into a water body; above this limit, water quality standards cannot be met. All point and nonpoint sources in a watershed, including agriculture, are subject to discharge limits established by TMDLs. Most TMDL programs in the United States operate at the state level and result from lawsuits filed against the EPA by environmental groups for failure to perform its mandatory duties under the CWA to identify and then improve water quality. As an example, in 1997 Delaware negotiated a TMDL agreement with EPA, established a 10-year schedule to develop TMDLs for affected waters, and agreed to implement pollution control strategies that ensure pollutant loadings are below TMDLs. The reductions in N and P loading necessary to meet TMDLs will involve intensive management efforts to control point and nonpoint sources of pollution. For example, elimination of all point-source discharges of N and P and major reductions in nonpoint loading of N (85%) and P (65%) are needed to meet the TMDL requirements for Delaware's Indian River. The Delaware TMDL agreement also requires a 20% reduction in atmospheric deposition of N, relevant to agriculture because of concerns about NH₃ emissions from the nearby poultry industry. Today, state and federal environmental and advisory agencies, university scientists, environmental organizations, and local "tributary action teams" are working with Delaware agriculture to identify cost-effective BMPs that can achieve TMDL goals.

The first significant step in changing U.S. national policy that directly targeted CAFOs and AFOs was the 1999 EPA-USDA "Unified National Strategy for AFOs." This document defined the guiding principles for a joint effort between the nation's lead regulatory agency (EPA) and its lead technical agency for agriculture (USDA) to address the water quality and public health impacts associated with AFOs. Following up on this strategy, in the summer of 1999 the USDA Natural Resources Conservation Service (NRCS) released a national nutrient policy, which requires implementation of NMPs and CNMPs for farmers receiving technical assistance and cost-sharing funds. In 2001, as mandated by a 1992 federal court-issued decree, the EPA initiated steps to update the regulations associated with the impacts of CAFOs on water quality. The stated reasons for this were that the livestock industry had undergone major changes during the previous 20 years, with a trend toward fewer and larger operations, and that this restructuring was causing an increased discharge of manure nutrients from CAFOs that contributed to pollution of the nation's waterways. After a series of public hearings and a long comment period, the final CAFO rule was promulgated in 2002.* Key provisions are (1) inclusion of land application of manures by CAFOs as a regulated activity; (2) requiring poultry, swine, and heifer CAFOs to obtain NPDES permits; (3) requiring all CAFOs to implement NMPs that use BMPs to protect water quality; (4) more stringent requirements for manure storage and record keeping.

* See <http://www.epa.gov/npdes/caforule> for detailed information on the background and requirements of the CAFO rule.

State and regional environmental policies affecting CAFOs and AFOs have also changed and in some cases state nutrient management laws are more restrictive than federal requirements. The state laws passed in the Mid-Atlantic region of the United States are some of the most comprehensive and are described here to illustrate state policy changes. The first law passed was Maryland's 1998 Water Quality Improvement Act (WQIA). Passage of this act was stimulated by public concerns over fish kills in rivers on the Eastern Shore of Maryland in the summer of 1997. These fish kills were reportedly caused by *Pfiesteria* spp., a toxic dinoflagellate that had been implicated in earlier, massive fish kills in North Carolina and also in human health problems. In response to a public outcry and intense media pressure, the Governor of Maryland appointed the "Citizens Pfiesteria Action Commission" in the autumn of 1997. The report of this commission led to legislation requiring all agricultural operations with annual incomes greater than \$2500, or more than eight animal units, to develop and implement N- and P-based NMPs. The legislation is wide ranging in scope, going beyond farming to include municipalities that apply biosolids to land, vegetable growers, nurseries, greenhouses, turfgrass producers, and some horse farms in its requirements (Simpson, 1998). The Maryland law, which passed in a politically charged atmosphere, stimulated similar efforts in Virginia and Delaware, under pressure from the EPA, to move away from the voluntary nutrient management practices advocated in the past and in the direction of regulated programs, especially for AFOs and CAFOs. In January of 1999, the Virginia legislature passed the Poultry Waste Management Bill that gave regulatory authority over poultry operations with more than 20,000 chickens to the Virginia Department of Environmental Quality and mandated P-based NMPs for some farms. In 1999, Delaware passed a state nutrient management act, similar in many respects to the Maryland WQIA (Sims, 1999). A Delaware Nutrient Management Commission (DNMC) was established to develop and implement a state NMP to protect and improve water quality. The law required a state education/certification program for all nutrient users, mandated "P-based management" for high-P soils, and led to a memorandum of understanding between the poultry industry and the DNMC that has fostered statewide efforts to better manage manure nutrients and to develop alternatives to land application of manures.

In summary, today, due to the transition from voluntary to regulatory approaches, nutrient management for AFOs/CAFOs is now a complex mixture of voluntary and mandatory NMPs and CNMPs: more regulatory limits on land application of manures and fertilizers; government subsidization of BMPs known to be successful; expanding research on innovations in nutrient management; and a rather fragmented assortment of government and private sector schemes to develop alternatives to land application of manures. It remains to be seen if these approaches will lead to animal production systems that are economically and environmentally sustainable.

8.2 NUTRIENT MANAGEMENT PRACTICES FOR NITROGEN

Efficiency can be defined as the ability to accomplish a task without the waste of time, energy, or resources. Nitrogen efficiency for a soil-plant system, in its simplest form, can be viewed as the ability to manage the time, energy, and resources needed to obtain an acceptable level of plant growth (the task) with minimal loss of N (the waste). Few, if any, natural systems are 100% efficient, and, given the complexity of the soil N cycle and the constraints imposed by time, labor, soil type, cropping practices, environmental conditions, and available resources, it is perhaps not surprising to find that efficiency values for N use in most cropping systems rarely exceed 60% and commonly range between 30 and 50%. Unfortunately, where N is concerned, inefficiency of recovery by one ecosystem (soil-plant) usually results in redistribution of some form of N (NO_3 , NH_3 , N_2O) to another sector of the environment, often with adverse effects.

The following sections outline currently accepted principles of efficient N management, primarily for agricultural crops, with some references to forest soils, horticultural operations, turf, and land reclamation given to illustrate key differences in N management in those settings.

8.2.1 General Principles of Efficient Nitrogen Management

Efforts to improve efficiency of N use by agricultural crops have addressed the agronomic and environmental aspects of this issue for more than 30 years. We have worked steadily to maximize agronomic efficiency by producing greater yields with less N, and to increase environmental efficiency by minimizing N loss from soils to ecosystems sensitive to N pollution. As part of this effort, concepts such as *yield efficiency* (YE) and *crop N recovery efficiency* (NRE) have been used to quantify success for existing, or proposed, N management programs.

$$YE = \frac{[\text{Crop yield}]_{+N \text{ Source}} - [\text{Crop yield}]_{\text{Soil alone}}}{\text{Total N added by N source}} \quad (8.1)$$

$$NRE = \frac{[\text{Crop N uptake}]_{+N \text{ Source}} - [\text{Crop N uptake}]_{\text{Soil alone}}}{\text{Total N added by N source}} \quad (8.2)$$

where $[\text{Crop Yield}]_{+N \text{ Source}}$ and $[\text{Crop N Uptake}]_{+N \text{ Source}}$ refer to the yield and total N uptake, respectively, by a crop that has received additions of either fertilizer or organic N, and $[\text{Crop Yield}]_{\text{Soil alone}}$ and $[\text{Crop N Uptake}]_{\text{Soil alone}}$ refer to the yield and total N uptake, respectively, by a crop grown in an unamended soil; these values represent the native soil N supplying capacity.

Example Problem 8.2

An on-farm strip trial experiment was conducted to calculate NRE for two methods to corn N fertilization: (A) applying all fertilizer N at planting, at 200 kg N/ha; (B) split applications of fertilizer N: 20 kg N/ha applied at planting, 100 kg N/ha applied by sidedressing, and 80 kg N/ha applied by fertigation. Crop N uptake was 120 kg N/ha for Method A and 180 kg N/ha for Method B. Crop N uptake was 60 kg N/ha in an unfertilized strip in the same field. Calculate NRE for the two methods using Equation 8.2. Explain the reasons for the differences in NRE.

$$NRE = [(\text{Crop N uptake})_{N \text{ source}} - (\text{Crop N uptake})_{\text{soil alone}}] / [\text{Total N added by N source}]$$

$$NRE\text{-Method A} = (150 \text{ kg N/ha}) - (60 \text{ kg N/ha}) / (200 \text{ kg N/ha}) = 0.45 = 45\%$$

$$NRE\text{-Method B} = (180 \text{ kg N/ha}) - (60 \text{ kg N/ha}) / (200 \text{ kg N/ha}) = 0.60 = 60\%$$

Yield efficiency considers only the relationship between N fertilization and crop production and is primarily an economic assessment. Nitrogen recovery efficiency provides an estimate of applied N that, because it was not taken up by the crop, has been redistributed to some other component of the N cycle. Crop NRE thus addresses economic and environmental concerns and, if combined with other data, such as changes in soil NO_3^- concentrations in the crop rooting zone, can help identify the fate of the unrecovered N. Several key points should be kept in mind when evaluating NRE values for differing crops and management practices. First, it is important to remember that unrecovered N is not necessarily lost from the soil–plant

system, but may be temporarily immobilized as organic N, remain in the rooting zone as NH_4^+ or NO_3^- , or even be recycled through irrigation waters. In these situations, the unrecovered N from one crop may be recovered through uptake by a subsequent crop. Second, as shown in Figure 8.4, the nature of crop response (yield and N uptake) will depend on the N rate selected and the method used to apply N (i.e., spring application vs. sidedressing). In general, YE and NRE decrease, and the potential for N loss to other ecosystems increases, as N rate goes up. However, by using a more efficient application method (sidedressing), crop N uptake, and thus NRE, can be increased. Finally, as most studies base NRE on the difference in N uptake between a fertilized crop and a nonfertilized control, it should be noted that applying N to a crop can affect uptake of native soil N, by altering soil N transformations, and enhancing the ability of crop roots to recover N.

The influences and interactions of agronomic factors (tillage, irrigation, rotation, manure use, method and timing of N application) on NRE have been quantified for many N sources, soil types, and crops (Table 8.7). The purpose of most studies has been to identify BMPs that can optimize crop N uptake, and thus the profitability of N use, and also to assess the relative magnitude of N losses as a function of environmental conditions and soil/crop management. More sophisticated research has attempted to determine the specific fate of applied N (Figure 8.5), often relying on the use of ^{15}N -labeled fertilizers or crop residues to trace the cycling and movement of N between soils, plants, waters, and the atmosphere.

Quantifying the environmental efficiency of N use, while clearly important, is less straightforward, primarily because of the difficulty in establishing direct linkages between agricultural management practices and polluted resources. Most studies have used the NRE approach and assumed that if a management system has low NRE values (high amounts of unrecovered N), and the potential to adversely affect the environment, the system requires improvement. If some direct measurement of N pollution in the geographic area dominated by the agricultural management system is also

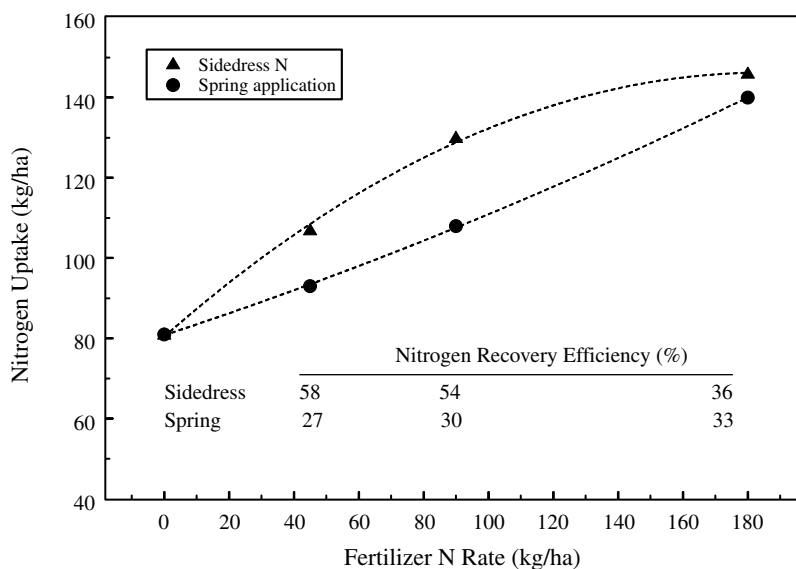


Figure 8.4 Nitrogen uptake and N recovery efficiency (NRE) for corn. Fertilizer N was either applied in a single spring application or in a split application using starter and sidedress fertilizers. (From Bock, B. R., in *Nitrogen in Crop Production*, R. D. Hauck, Ed., American Society of Agronomy, Madison, WI, 273–294, 1984. With permission.)

Table 8.7 Representative Values for N Use Efficiency of Corn

Nitrogen Rate (kg/ha)	Treatments Studied and N Recovery Efficiency (%)	
Delaware	Poultry Manure	NH₄NO₃
84 ^a (107 ^b)	50	62
168 (214)	33	57
252 (321)	34	50
Maryland	Minimum Tillage	Plow Tillage
90 ^a	53	67
80	53	52
270	53	38
Vermont	Dairy Manure + NH₄NO₃	NH₄NO₃ Alone
0 ^a (243 ^b)	41	—
56 (243)	35	97
112 (243)	18	93
168 (243)	16	68
Wisconsin	Biosolids: Site 1	Biosolids: Site 2
340 ^b	17	21
680	19	17
1360	12	10
2720	9	6

Note: Nitrogen use (recovery) calculated using the approach described in Section 8.2.

^a Rates of NH₄NO₃ added.

^b Total amount of N added in manure or biosolids.

Source: Adapted from Sims, 1987 (Delaware); Meisinger et al., 1985 (Maryland); Jokela, 1992 (Vermont); Kelling et al., 1977 (Wisconsin).

available (e.g., high NO₃⁻ concentrations in drinking water wells), then the pressure to modify the system is particularly great.

An example of such a scenario would be the use of poultry manure in crop production on the Delmarva peninsula (Delaware–Maryland–Virginia), where data from well surveys indicated widespread contamination of shallow groundwater wells with NO₃⁻ (Figure 8.6a). The soils in the region are coarse textured and well drained, rainfall is plentiful (~100 cm/year), and the use of overhead irrigation is increasing. The area has one of the most highly concentrated poultry industries in the world (Figure 8.6b), and agriculture is dominated by crops with high N requirements (corn, small grains). Laboratory studies showed that poultry manure N was rapidly converted to NO₃⁻ in most soils, field studies with irrigated corn found NRE values of 20 to 50%, and monitoring studies of wells in manured fields found NO₃⁻ concentrations above current EPA drinking water standards (10 mg NO₃-N/L). Although it was recognized that other sources, primarily N fertilizers and rural septic systems, contributed to groundwater NO₃⁻, the potential for the poultry-based agriculture of the area to contaminate groundwaters and surface waters resulted in intensive efforts by advisory and regulatory agencies to improve crop N management in general, and manure management in particular. Many of the approaches used to improve N use efficiency on Delmarva, such as mandatory CNMPs, innovative soil and plant N tests, better fertilizer and manure management, soil conservation BMPs (e.g., winter

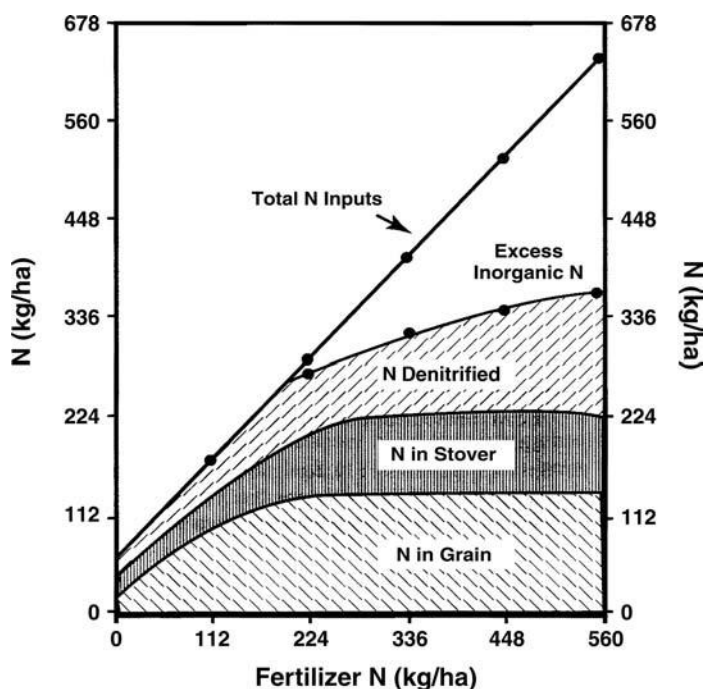


Figure 8.5 Influence of N rate on the fate of fertilizer N. (From Boswell, F. C. et al., in *Fertilizer Technology and Use*, O. P. Engelstead, Ed., American Society of Agronomy, Madison, WI, 229–291, 1985. With permission.)

annual cover crops and buffer strips to recover residual $\text{NO}_3\text{-N}$ by plant uptake and constructed wetlands to enhance denitrification), and alternative uses for animal manures are discussed in the next section.

In summary, improving the efficiency of N management will require an integrated approach, often regional in nature. Traditional approaches have combined the development and implementation of research-based BMPs for soil conservation and nutrient management with long-term basic research on the soil N cycle (Table 8.8). Recently, intense environmental pressures to control N pollution have raised the issue of mandatory, legislated controls on fertilizer and manure N use, similar to the approach now used for biosolids. For example, the EU has adopted a “Nitrate Directive” that mandates designation of $\text{NO}_3\text{-}$ vulnerable zones (NVZ; all areas of land where agricultural sources contribute to $\text{NO}_3\text{-}$ pollution of waters) in 15 of the member countries. Within the NVZ, mandatory measures limit when and at what rate N sources can be applied. For example, the maximum amount of manure N that can be applied or deposited by grazing animals in a NVZ each year is 170 kg/ha. In 2001, about 37% of the total EU land surface was either designated or scheduled to be designated as a NVZ. In some cases, entire countries are NVZ (Austria, Denmark, Finland, Germany, the Netherlands), while in other countries certain regions, such as those with intensive livestock production, are NVZ.

The following sections describe practices designed to improve N efficiency in agriculture, although most apply equally well to nonagricultural settings. Nonpoint N pollution reflects the combined effect of farms, urban areas, municipal and industrial by-product disposal sites, land reclamation projects, and rural septic systems. Given this, a broad perspective, combined with diverse BMPs that address all land uses in watersheds and airsheds, is fundamental to our efforts to develop NMPs that sustain agricultural profitability and protect the environment.

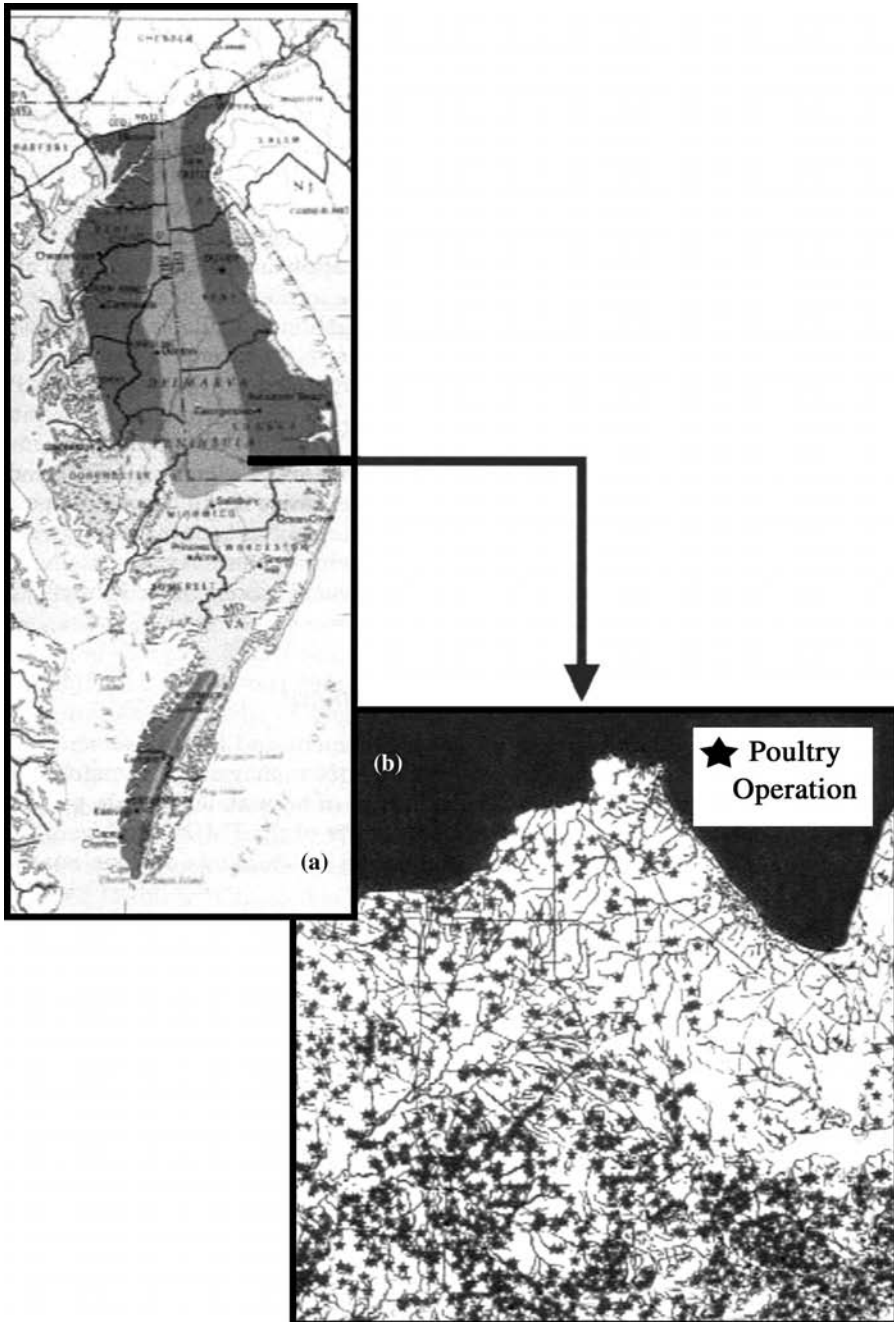


Figure 8.6 (a) Areas on the Delmarva peninsula with elevated $\text{NO}_3\text{-N}$ concentrations in groundwater. Areas with darkest shading commonly have $\text{NO}_3\text{-N}$ concentrations near or exceeding the U.S. EPA standard for drinking water (10 mg $\text{NO}_3\text{-N/L}$). (Adapted from Hamilton, P.A. and R.J. Shedlock, U.S. Geol. Surv. Circ. 1080, Denver, CO, 15 pp., 1992.) (b) Geographic intensification of poultry production in Sussex County, DE. Each star represents a poultry operation with two or more poultry houses. (From Cabrera, M. L. and J. T. Sims, in *Beneficial Uses of Agricultural, Municipal, and Industrial By-Products*, J. Power and W. A. Dick, Ed., SSSA, Madison, WI, 425–450, 1999. With permission.)

Table 8.8 Summary of Best Management Practices (BMPs) for Efficient N use

Management Approach	Examples and Comments
Soil, Crop, and Water Management	
Soil and water conservation	Contour plowing, terracing, reduced tillage, improved irrigation management; all act to reduce erosion, runoff, and leaching of N.
Cropping sequence and cover crops	Rotating legumes and nonlegumes to reduce need for N fertilizers; legumes and winter annual cover crops can “scavenge” residual soil N; benefits from crop rotations include economic stability, erosion control, reduced pest and disease pressure.
Watershed management	Soil and water conservation and nutrient management supported by widespread educational programs, cost-sharing, and guidelines or regulations on irrigation, fertilizer use.
Nutrient Management	
Soil, plant, and waste testing	Recent advances in soil and plant N testing (e.g., the PSNT, LCM) provide opportunities for more efficient use of fertilizers and manures.
Application timing and method	Split applications of N, fertigation, slow-release fertilizers, injections and deep placement of volatile N fertilizers; all directed toward improving synchrony between N availability and crop N uptake pattern.
Fertilizer and waste technology	Nitrification and urease inhibitors improve efficiency of fertilizer N recovery; composting and pelletizing stabilize N in organic wastes and provide materials that can be handled and applied more efficiently.
Fundamental Changes in Agriculture	
Legislation	Regulations, not guidelines, mandate amount and timing of N application from fertilizers or organic wastes; farm-scale nutrient budgets require farmers to find alternative uses for excess manure; most approaches are voluntary at present but legislation affecting nutrient management has been introduced and/or passed in several states.
Genetic advances	Genetic alteration to introduce biological N fixation ability into nonlegumes (corn, wheat); increase N fixation capacity of legumes; advances in genetic manipulation of plants make these long-term goals of basic research in N fixation more feasible.
Cropping patterns	Increased use of legumes, decreased production of cereal grains; more legumes would reduce fertilizer N use, but likely affect economics of production, dietary habits of consumers; pressures to convert to low-input, “sustainable” agriculture with less reliance on fertilizers and pesticides; low-input agriculture often labor-intensive, while the availability of farm labor is already inadequate in many urban societies; loss of cropland due to urbanization, desertification; as food production is highly dependent on amount of arable land, major losses of cultivated acreage would increase pressure to obtain higher yields on remaining land, requiring higher inputs, and increasing potential for nonpoint-source pollution; many urban areas and areas of intense animal production already have inadequate land available to use organic wastes they currently produce.

Source: Adapted from Keeney, 1982.

8.2.2 Assessing Soil Nitrogen Availability

Current approaches to N management in agricultural cropping systems normally begin with an assessment of the crop N requirement at a realistic yield goal, relative to the native capacity of the soil to provide plant-available N through mineralization of soil organic N. Fertilizer or organic by-product management practices, based on local soil and climatic conditions, are then relied on to

provide any additional N needed to obtain optimum yields and to minimize N losses. The amount of supplemental N needed by a crop is related to the potential for excess N in the soil by the following equation, referred to as a soil nitrogen budget:

$$N_f = [N_{up} + N_{ex}] - [N_{som} + N_{na}] \quad (8.3)$$

where

N_f	=	amount of N needed from fertilizer, manure, etc.
N_{up}	=	crop N requirement at desired yield
N_{ex}	=	excess N lost by denitrification, erosion, leaching, or volatilization; varies as a function of the efficiency of each soil-crop system
N_{som}	=	N added from mineralization of soil organic matter, crop residues, previous applications of organic by-products, etc.
N_{na}	=	natural additions of N (rainfall, irrigation, atmospheric deposition)

Minimizing N_{ex} , therefore, requires that we do not overestimate crop yield potential for a particular soil, and thus both N_{up} and N_f , the crop N requirement and amount of fertilizer needed to attain a realistic yield. Nor should we underestimate the potential of the soil or other natural sources of N (N_{som} , N_{na}) to provide a significant percentage of N_{up} . Unfortunately, there are many examples where both types of errors have occurred, frequently resulting in groundwater contamination by NO_3^- .

The issue of overapplication of N is complicated not only by overly optimistic estimates of potential yield, but also by the relatively inexpensive nature of fertilizer N, and, when manures and biosolids are involved, the continuing pressure to dispose of organic by-products, regardless of the true N requirement of the crop. The relationship between unrealistic yield goals and potential for groundwater contamination is clearly shown in Figure 8.7 for irrigated corn production in Nebraska, and the potential for a serious imbalance in a regional N budget is illustrated in Table 8.9 for the poultry and commercial fertilizer industries in Delaware.

In addition to overestimates of N_f , another serious problem for N use efficiency (NUE) has been the failure to develop reliable tests for available soil N and N added in organic by-products so that farmers can accurately adjust fertilizer N rates to compensate for what the soil and organic amendments will provide during the crop's growing season. An accurate soil test for N has been a long but elusive goal for soil scientists. The complex and dynamic nature of N cycling and its extreme sensitivity to often unpredictable climatic factors, such as temperature and rainfall, have made it difficult to use chemical extractants to estimate N availability in advance of planting as is commonly done for other plant nutrients (e.g., P, K, Ca, Mg, Mn, Cu, and Zn). Similar problems have prevented adoption of rapid chemical tests for available N in organic by-products.

Some advances in soil N testing have occurred. One of the most significant was the development, in 1984, of the "pre-sidedress soil nitrate test" (PSNT). The PSNT was conceived and first evaluated by F. R. Magdoff of the University of Vermont to address the problem of overfertilization of corn with N in the northeastern United States, particularly in fields with histories of manure and legume use. The PSNT has four basic tenets, briefly summarized as follows: (1) all fertilizer N for corn, except a small amount banded at planting, should be sidedressed (banded next to the growing crop) when corn enters the period of maximum N uptake; (2) soil and climatic conditions prior to sampling integrate the factors influencing the availability of N from the soil, crop residues, and from previous applications of organic by-products; (3) a rapid sample turn-around (<14 days) by a soil testing laboratory is possible; and (4) farmers will normally not sample to a depth >30 cm. The PSNT has since been evaluated in more than 300 field studies in the northeastern and midwestern United States and has been repeatedly shown to be successful in identifying N sufficient soils (Figure 8.8a).

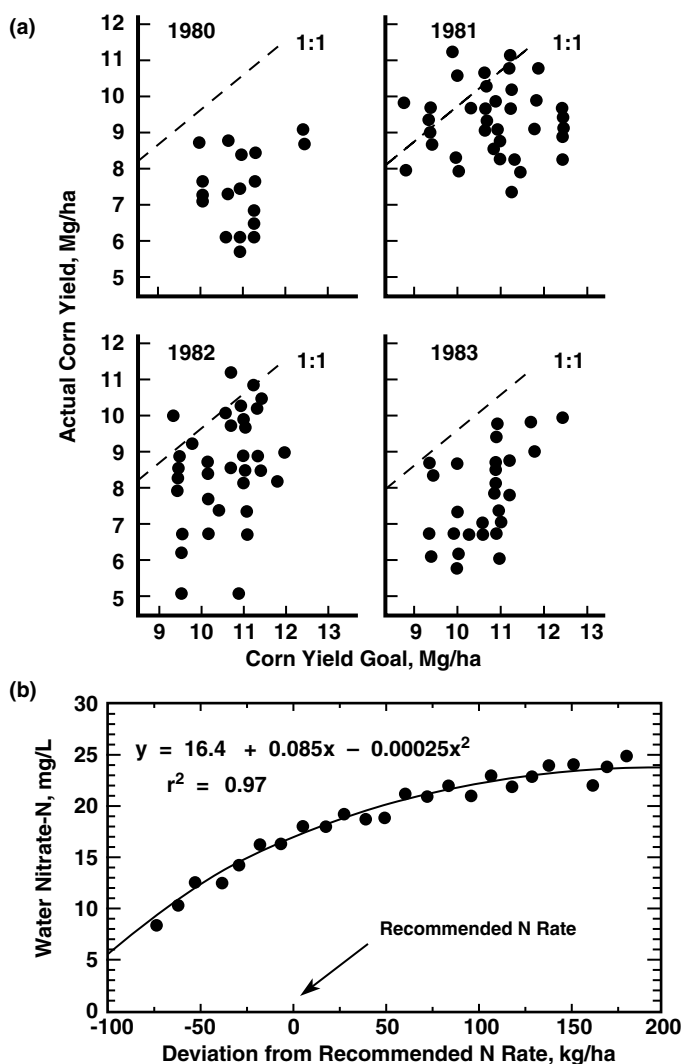


Figure 8.7 (a) Comparison of farmer yield goals for irrigated corn with actual yields obtained. Dashed line indicates 1:1 fit between yield goal and actual yield. (From Hergert, G. W., in *Soil Testing: Sampling, Correlation, Calibration, and Interpretation*, J. R. Brown, Ed., SSSA Spec. Pub. 21, Soil Science Society of America, Madison, WI, 1987. With permission.) (b) Influence of deviation from recommended N rate on groundwater nitrate concentrations in Nebraska. (From Schepers, J. S. et al., *J. Environ. Qual.*, 20, 12–16, 1991. With permission.)

The potential value of the PSNT in reducing nonpoint N pollution is clearly illustrated in Figure 8.8b, which provides results of 366 soil samples collected in Sussex County, Delaware by advisory agency staff as part of a cost-sharing program to promote use of this test. About 55% of the PSNT samples had values >20 mg/kg, where no additional sidedress fertilizer N would be required and, where sidedress N was needed, recommendations by advisors were consistently lower (average of 32 kg N/ha) than those planned by farmers (average of 67 kg N/ha). Widespread adoption of the PSNT, however, has been limited by logistical difficulties. The greatest obstacle has been the need to obtain a PSNT soil sample at a very busy time of year for farmers, who are often planting, cultivating, and applying herbicides at the time

Table 8.9 Nitrogen Mass Balance for Delaware and Sussex County, DE^a

Nitrogen Produced or Sold vs. Crop Nutrient Requirements	Nutrient Available or Required (Mg/yr)	
	Statewide	Sussex County
Nitrogen Produced or Sold: Sources		
Commercial fertilizers	20,680	10,520
Poultry litter/manure	14,270	12,625
Other manures	1,180	390
Municipal biosolids	825	275
Total N produced or sold	36,955	23,810
Nitrogen Inputs Needed for Optimum Crop Yields		
Corn	8,500	5,170
Soybeans	0	0
Wheat	3,175	1,725
Barley	1,375	680
Sorghum	580	220
Processing vegetables	2,790	1,270
Fresh-market vegetables	880	400
Hay	680	230
Total required by all crops	17,980	9,695
Annual Nutrient Balance		
Mg per state or county	18,975	14,115
kg N/ha	84	140

^a Sussex County, DE is the site of Delaware's poultry industry. The county has approximately 100,000 ha of cropland and produces about 230 million chickens each year.

Source: Beegle, et al., in *Agriculture, Hydrology, and Water Quality*, P. Haygarth and S. Jarvis, Eds., CAB International, Oxon, U.K., 2002. With permission.

PSNT samples need to be collected. The development of NO_3^- “quicktest” kits and NO_3^- sensitive electrodes that can be used in the field have made the PSNT more acceptable to farmers and their advisors.

A recent advance in soil N testing may help to overcome some of the logistical problems of the PSNT. The “amino sugar N test,” developed in the Midwest, has shown potential as a rapid, cost-effective means to identify soils that are “nonresponsive” to N. The test uses rapid analysis of a soil organic N fraction (amino sugar N) that seems to be a major source of plant-available soil N. The main advantage of this test is that it is done on the same soil sample collected in advance of planting for other soil fertility tests (e.g., lime, P, K). This eliminates a major concern with the PSNT and gives farmers more time to develop N management plans for manures and fertilizers based on the N-supplying capacity of their soils. In 25 field studies in Illinois, the amino sugar soil N test accurately separated sites that were “responsive” and “nonresponsive” to N fertilization (Figure 8.8c).

Even more encouraging are the results of research with the leaf chlorophyll meter (LCM) that showed this extremely rapid, in-field measurement of leaf “greenness” was as accurate as the PSNT in identifying N-sufficient sites (Figure 8.9a). Another new approach to assess N sufficiency for corn is the late-season stalk nitrate test (Figure 8.9b). This “postmortem” test uses the concentration of NO_3^- in the lower portion of the stalk at corn maturity to identify fields that received excessive

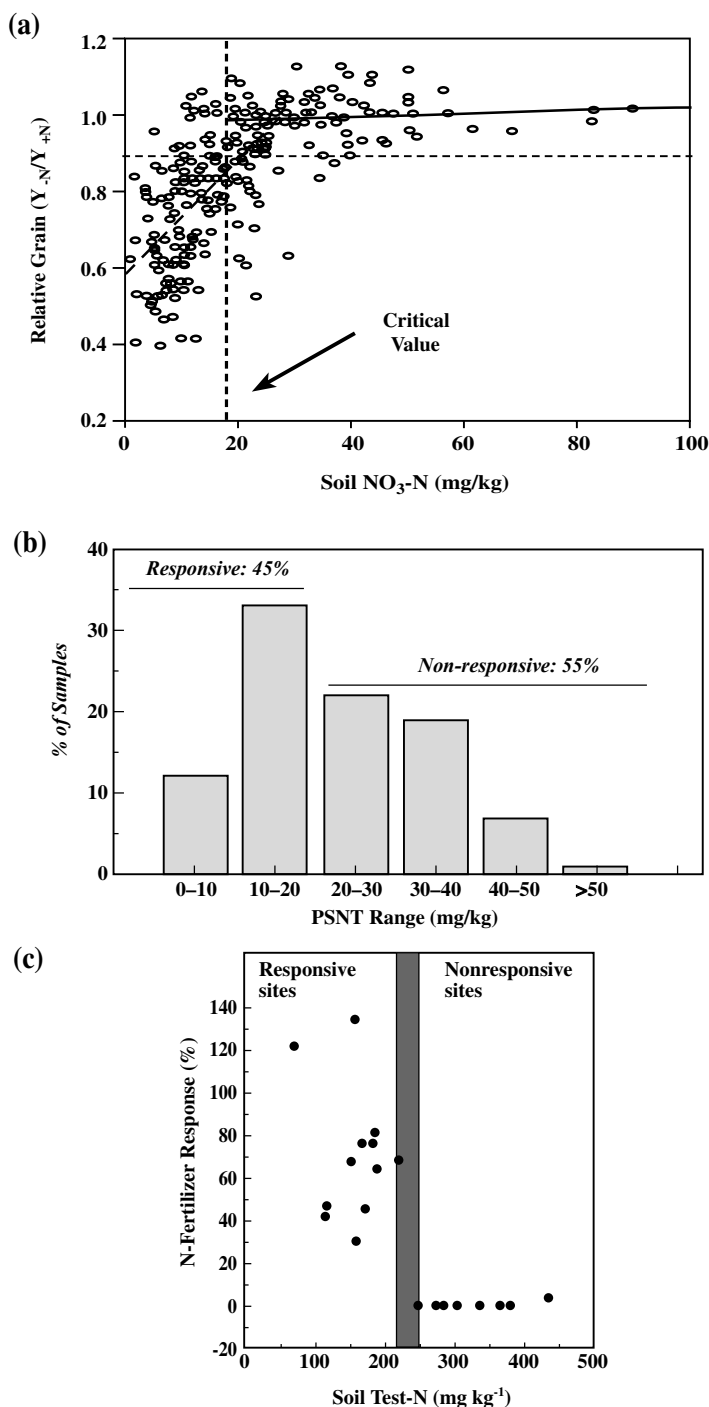


Figure 8.8 Illustration of the use of soil and plant N testing procedures to identify N-sufficient soils. (a) Relative yield of corn (Y_{-N} , yield in control (0 N) treatment, divided by Y_{+N} , yield from adequately fertilized treatment) vs. soil nitrate (0–30 cm) in the late spring. (Adapted from Magdoff et al., 1990.) (b) Percentage of PSNT samples collected by advisory agency staff in Sussex County, Delaware where response, or non-response, of corn to sidedress fertilizer N would be expected. (From Sims, J. T. et al., *Water Sci. Tech.*, 39, 291–298, 1999. With permission.) (c) Relationship between amino sugar soil test N and N fertilizer response for soils from 25 N-response experiments in Illinois. (From Khan, S. A. et al., *Soil Sci. Soc. Am. J.*, 65, 1751–1760, 2001. With permission.)

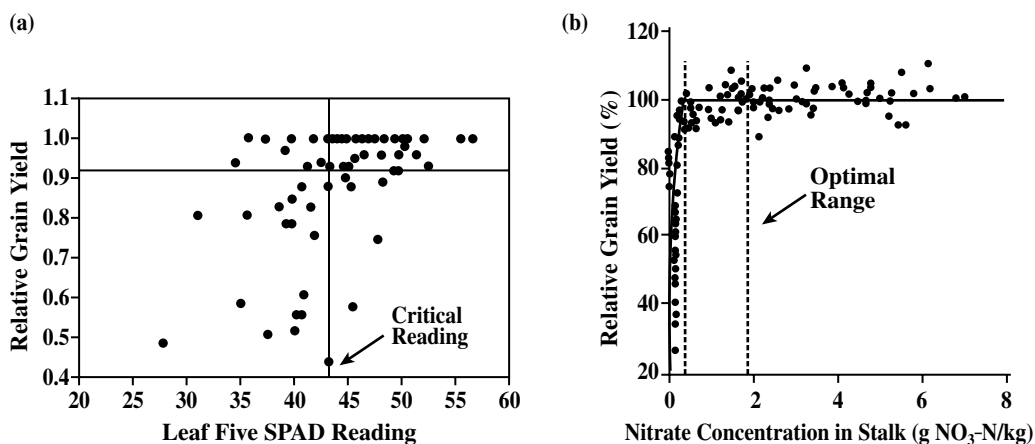


Figure 8.9 Evaluation of new “quicktests” for plant N. (a) Relative yield of corn vs. leaf chlorophyll meter reading taken in late spring (SPAD refers to type of meter used for reading). (From Piekielek, W. P. and R. H. Fox, *Agron. J.*, 84, 59–65, 1992. With permission.) (b) Relative yield of corn vs. nitrate concentration in the lower portion of cornstalk at maturity. (From Binford, G. D. et al., *Agron. J.*, 82, 124–129, 1990. With permission.)

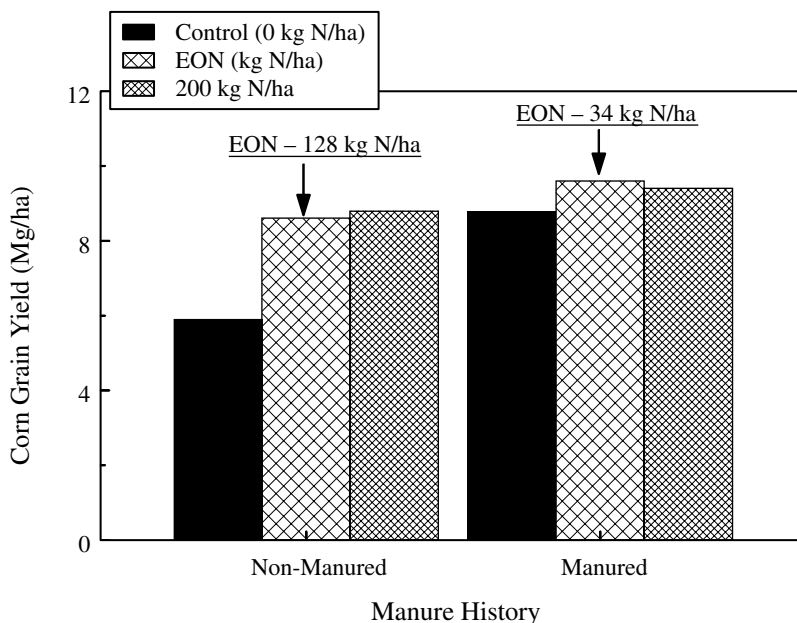


Figure 8.10 Yield response of corn to economically optimum N (EON) rates in fields with and without a history of manure applications. Numbers in bars are average yields, in Mg/ha, of all nonmanured or manured sites at EON rate. (From Roth, G. W. and R. H. Fox, *J. Environ. Qual.*, 19, 243–248, 1990. With permission.)

N from fertilizers or manures. As with the PSNT, collection of stalk samples has proved to be an obstacle to adoption of this N test. Fortunately, research has shown that late-season LCM readings may be as accurate as the stalk nitrate test. If so, this would greatly decrease the logistical problems of late-season N testing and increase the use of this approach to monitor the success of an N management program.

Development and field evaluation of soil and plant N tests further illustrate the need for farm and regional NMPs. For example, studies investigating soil/plant N tests in fields regularly amended with animal manures have often found little or no N may be required to attain optimum yields, even when manure was not applied in the current year. This is shown in Figure 8.10 where the *economically optimum N* (EON) rates (the N rate where economic return on fertilizer N investment is maximized, based on assumed fertilizer costs and crop prices) are compared for 11 fields with and without long histories of manure use. The EON rates for manured and nonmanured fields were 34 and 128 kg N/ha, respectively, reflecting the greater N-supplying capacity of regularly manured soils. The identification, by soil/plant N tests, of a reduced need for fertilizer N in a field is an economic benefit to farmers; however, it also means that manure N applications are not needed or can be reduced. If soil/plant N tests are part of a CNMP, they can help to quantify the amount of excess manure on a farm that should be diverted to other fields or off-farm uses, if such alternatives are economically viable.

8.2.3 Nitrogen Sources and Application Methods

Once the need for and rate of supplemental N have been determined, either through soil and plant testing or a general knowledge of the cropping system, the next considerations are the source of N to be used and the method and timing of N application. Maximization of N efficiency requires that the best N source be applied in as timely a manner as possible, often through the use of multiple applications (see Section 5.2.5 for discussion of basic properties of inorganic and organic N sources). The primary consideration in selection of an N source is often economics, beginning with cost per unit of N. Other factors that influence the total cost of the N source include availability of the material (transportation costs), storage and handling (equipment and application costs), crop-specific fertilization requirements (e.g., the need for a mixed fertilizer), and any properties of the fertilizer material that may significantly affect its efficiency in the cropping system used. In animal-based agriculture where manure is constantly produced, other costs arise, such as the need for manure analysis, manure storage and treatment (e.g., lagoons, storage barns, composting facilities), the need for specialized application equipment, and greater time requirements and fuel costs for manure application relative to commercial fertilizers.

Selection of an N source can rarely be separated from selection of an N application method. Typical methods used to apply N fertilizers include *broadcasting*, *banding*, *injection*, and *fertigation*. *Broadcasting* refers to uniform applications of fertilizer materials to the soil surface, either as solid granules or pellets or in a liquid spray. The broadcast fertilizer may then remain on the surface (no-tillage crops, turf, forages) or be incorporated by a tillage operation such as disking or plowing. Broadcast applications made to a growing crop are referred to as *topdressing*. *Banding* is the placement of fertilizer N in a narrow band and can be done at planting; for row crops, banding fertilizers after crop emergence is referred to as *sidedressing*. Band applications of N at planting normally use N-P “starter” fertilizers with placement of the fertilizer approximately 5 cm below and 5 cm to the side of the seed to avoid salt injury to young seedlings. Banding at planting places an initial supply of N and P in a zone highly accessible to young root systems, and is particularly useful in no-tillage soils where cooler soil temperatures often delay initial root growth and nutrient uptake. Sidedress applications of N fertilizers can be done through injections, surface bands, sprays, or “dribbles.” *Injection* is the placement of fertilizer in the soil through specialized subsurface application equipment and is most commonly used for anhydrous NH_3 and liquid fertilizer materials such as urea-ammonium-nitrate (UAN) solutions. Fertilizer injections are normally made at deeper depths than band placements, particularly for anhydrous NH_3 , which reverts to a gas following injection and can be lost from the soil via volatilization if not placed correctly. *Fertigation* refers to the application of soluble N in irrigation waters and is not the same as *foliar fertilization* where fertilizers are sprayed directly on plant foliage. Only a few types of N fertilizers are suitable for

fertigation, due to the high degree of solubility and purity required to ensure complete dissolution and avoid clogging application equipment. Urea-ammonium-nitrate solutions are normally preferred over anhydrous or aqua NH_3 , which have higher volatilization potentials. Fertigation is most often used with overhead sprinklers or drip irrigation systems.

The method of application selected for an organic N source depends primarily on its physical properties. Solid organic by-products are usually applied by large flail or spinner spreaders, although recent advances in by-product processing, such as pelletizing, have increased the flexibility available to applicators. Liquid organic by-products are either injected or applied through wastewater irrigation systems. Incorporation of organic by-products may be mandated to avoid potential runoff of nutrient-rich solids or soluble organic materials into streams and lakes.

One of the most critical aspects of NUE is the timing of N application relative to crop N uptake. Most crops, particularly annual crops, have well-defined patterns of N accumulation, as illustrated for corn in Figure 8.11a. Fertilizer application techniques that deliver supplemental N in close synchrony with N uptake will, in general, be the most efficient, particularly on soils highly sensitive to N losses. A generalized ranking of the relative efficiency of the most common N application techniques would be fertigation > banding ~ sidedress > surface broadcast. The greatest efficiency

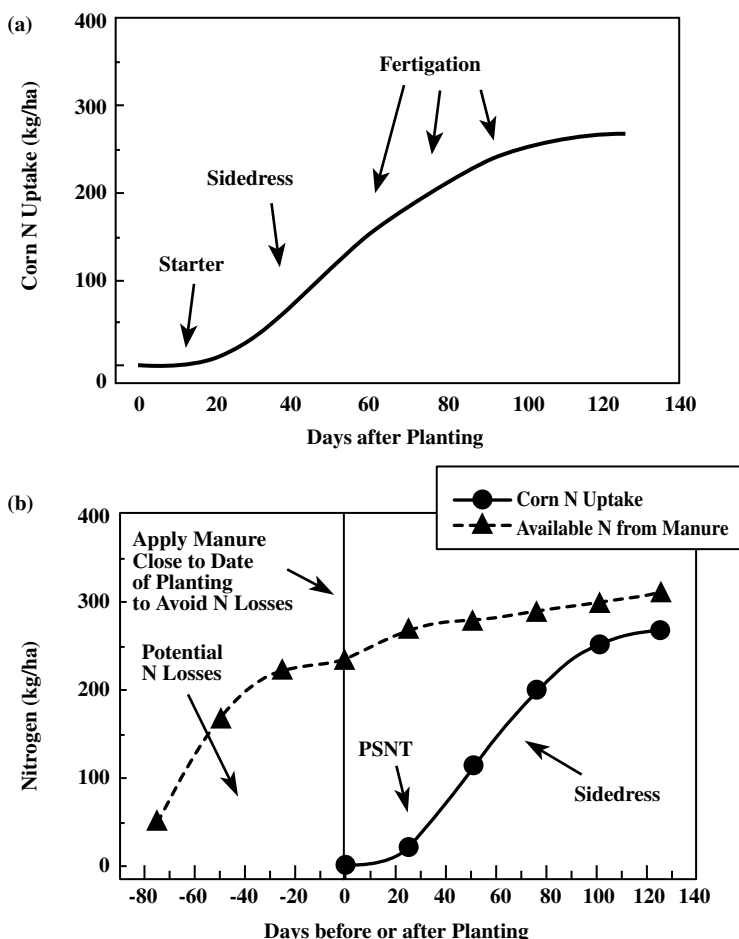


Figure 8.11 (a) Generalized representation of seasonal N uptake pattern for corn (kg/year), illustrating an efficient combination of N fertilizer techniques. (b) Nitrogen pattern for corn combined with typical rate of N release from poultry manure, showing the potential for N losses from poorly timed manure applications and the timing of the PSNT, relative to sidedress N application.

of N application normally results when several application techniques are combined. For irrigated corn this might involve a small amount of fertilizer N applied at planting, a sidedress application providing ~30 to 40% of the N requirement immediately prior to the period of most rapid N uptake, and several fertigations to supply the remainder of the crop requirement (Figure 8.11a). In a similar situation using organic by-products, this could involve a low (sub-optimum N rate) application rate of manure shortly before planting, followed by use of the PSNT to identify the sidedress fertilizer N requirement (Figure 8.11b). There are many situations, however, where serious limitations to improved timing of application of an N source exist. One such limitation is the amount of time required for delayed or multiple applications of N during the part of the growing season when many other operations must be performed in a timely manner, including tillage, planting, herbicide application, harvest of other crops, and installation of irrigation systems. For many farmers, applications of fertilizer or manure N during fall and winter months would be preferred, primarily because of the greater amount of free time available in this part of the year. Manure applications are also often preferred during fall or winter because the dry or frozen nature of soils at this time can reduce the amount of soil compaction and erosion caused by heavy equipment, relative to wet, spring conditions. However, the low efficiency of N recovery in these periods, because of leaching and denitrification losses prior to crop growth in the spring and summer, makes fall applications undesirable both economically and environmentally.

The basic reason that applications far in advance of crop N uptake are undesirable is the rapid rate of nitrification in most soils. The NH_4^+ applied in most fertilizers or manures is normally converted in soils to NO_3^- within a short period of time and is subject to leaching or denitrification losses prior to the initiation of crop uptake. One means to improve N use efficiency is to delay the process of nitrification by the use of chemical inhibitors applied in conjunction with N fertilizers or organic by-products, as shown in Figure 8.12. Chemicals such as nitrapyrin and thiosulfate have

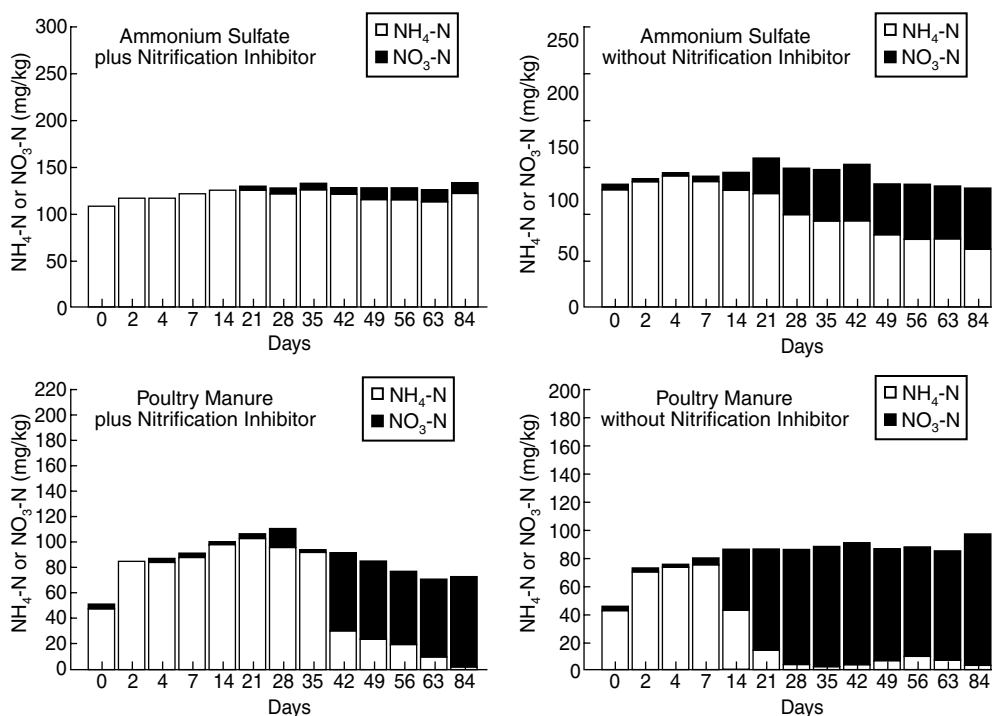


Figure 8.12 Illustration of the influence of a nitrification inhibitor (thiosulfate) on the rate of nitrification of an inorganic N fertilizer (ammonium sulfate) and an organic N fertilizer (poultry manure). (From Sallade, Y. E. and J. T. Sims, *Plant Soil*, 147, 283–291, 1992.)

been shown to inhibit the activity of nitrifying organisms, keeping applied N in the less leachable, ammoniacal form and increasing the possibility of crop N uptake. Slow-release fertilizer N sources achieve the same goal by physically sealing NH_4^+ within a resin, wax, or coating of sulfur, delaying dissolution of fertilizer granules and, by doing so, nitrification.

8.2.4 Soil and Water Conservation Practices for Nitrogen

Nitrogen use efficiency can be improved by means other than soil and plant testing, source selection, and management of application methods. Most soil and water conservation BMPs do not completely prevent N loss; instead, they provide options regarding where N lost from agricultural soils will end up, i.e., in groundwaters, surface waters, or the atmosphere. For example, using conservation tillage can reduce erosion losses of particulate forms of N, but has also been shown to increase infiltration and thus $\text{NO}_3\text{-N}$ leaching. No-till may also enhance $\text{NO}_3\text{-N}$ leaching by creating more preferential flow pathways in soils, such as earthworm and root channels. Surface applications of manure or other organic N sources, as in reduced tillage or pasture settings, can also reduce soil-N source contact and accelerate drying of organic materials. This will enhance NH_3 volatilization and decrease the rate of N mineralization. Together these factors result in a lower potential for $\text{NO}_3\text{-N}$ leaching but a greater likelihood for atmospheric impacts of NH_3 .

Other BMPs that have the potential to reduce N losses to groundwaters or surface waters are more efficient irrigation practices (e.g., drip vs. flood) designed to reduce $\text{NO}_3\text{-N}$ leaching; use of winter cover crops to trap residual $\text{NO}_3\text{-N}$ remaining in soils after crop harvest; and controlled drainage systems or artificial wetlands to enhance denitrification in field border areas. Again, note that enhancing denitrification does not prevent N loss; it simply transfers the N to another sector of the environment, the atmosphere, that is also sensitive to N pollution. Finally, recent advances in the use of remote sensing to assess plant N status and spatial variability in soil organic matter, moisture, and temperatures offer opportunities to identify areas where improved source management and soil and water conservation BMPs will have the greatest effect at preventing N loss (Power et al., 2000).

8.2.5 Nitrogen Management in Nonagricultural Settings

Nitrogen fertilizers and organic N sources are widely used in situations that differ greatly from production agriculture, such as land reclamation, road construction, urban and commercial horticulture, and forestry. Each of these end uses has its own constraints with regard to N use efficiency. Some are related to differences in the nature of the N cycle in natural, disturbed, or heavily amended soils, and others to the economics, politics, and logistics of soil-plant management. Reclamation and construction projects normally aim to produce a perennial, low-maintenance ground cover that requires the use of N fertilizers only initially, or in small, infrequent applications. Horticultural situations (greenhouses, nurseries, turf, ornamentals) are more intensive in nature and, because of the high cash value of the plants involved, rely heavily on fertilizer, often with less concern for economic or environmental efficiency of N use. Forest fertilization with N is most common in the commercial forestry industry and is an intermediate situation between low N input reclamation/res-toration projects and high N input horticulture.

Organic N sources are commonly used in both of these nonagricultural settings, for several reasons. The organic matter provided by biosolids, composts, and animal manures is often used in reclamation projects to provide a range of plant nutrients and to improve the poor physical properties of highly disturbed soils (see Chapter 3). In some cases these materials are stabilized with lime; thus they also can solve soil acidity problems (see Chapter 3). Greenhouses use high-organic-matter, “soilless” media almost exclusively to provide a light, well-aerated growth medium with high moisture holding capacity. Both situations have been considered good end uses for municipal organic by-products, such as biosolids and composts, because they mainly use nonfood-chain plants, and thus concerns about dietary accumulations of potentially toxic by-product

constituents (e.g., heavy metals) by humans are reduced. Recently, however, some questions have been raised about the impacts of by-product constituents on wildlife, domestic animals grazing on reclaimed sites, and soil microorganisms.

Management of soil, fertilizer, and organic N in land reclamation and forestry situations begins with an understanding of the differences that can occur in N cycling and plant growth, relative to cultivated soils. These differences can be fundamental or practical in nature. At the most basic level, microorganisms responsible for key N transformations such as mineralization, nitrification, and denitrification may be less efficient, inactive, or nonexistent in soils that have extreme physical or chemical properties, such as highly acidic mine spoils or pine forests. From a practical standpoint, amending these soils with fertilizer, organic N, or even small, intermittent doses of N as acid rain, can alter the activities of soil microbes and change the nature of N cycling, as seen in Figure 8.13 for nitrification in biosolids-amended forest soils and in Table 8.10 for nitrification and denitrification in acid mine spoils.

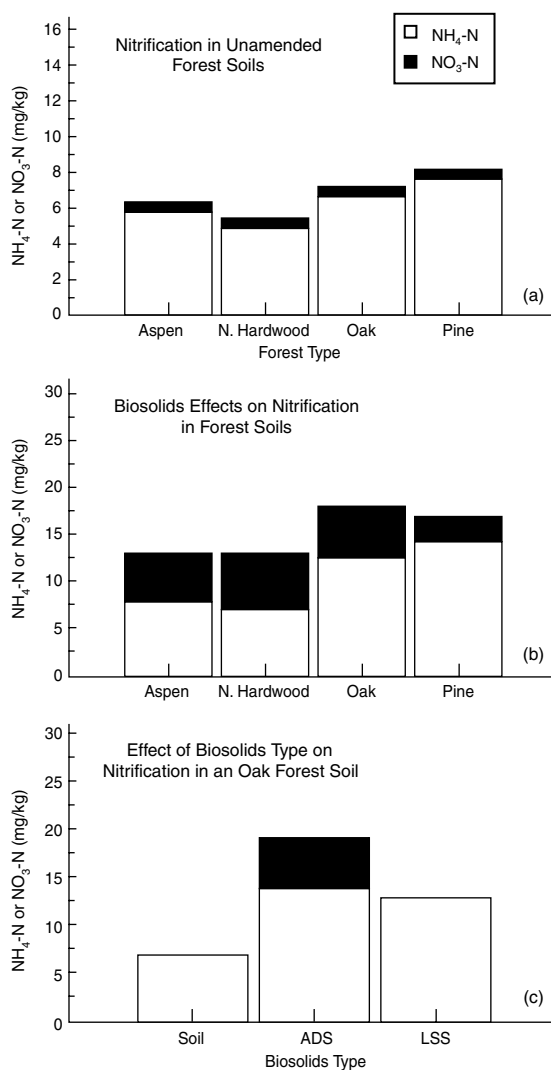


Figure 8.13 Nitrification in forest soils. (a) Effect of forest type on nitrification in unamended forest soils. (b) Amending forest soils with sludge increases nitrification. (c) Sludge type affects extent of nitrification in an oak forest (ADS = anaerobically digested sludge, LSS = lime-stabilized sludge). (From Burton, A. J. et al., *J. Environ. Qual.*, 19, 609–616, 1990. With permission.)

Table 8.10 Effect of Amending Highly Acidic Mine Spoils in West Virginia on Nitrification, Denitrification, and Populations of NO₃-Reducing Bacteria

Mine Spoil	pH	N Mineralization Potential ^a		Denitrification Parameters ^b	
		NH ₄ -N	NO ₃ -N	DEA	MPN
		— µg N/kg/h —		µg N/kg/h	MPN/g
Bald Knob					
Unamended	3.8	21	3	5	3
Amended ^c	6.8	−12	38	11	180
Osage					
Unamended	2.7	33	8	11	6
Amended ^c	5.2	−8	21	68	980

^a Rate of change in NH₄-N and NO₃-N in mine spoil materials in a 30-day laboratory incubation study.

^b Rate of denitrification of added NO₃ from mine spoils as determined in laboratory study of denitrifying enzyme activity (DEA). MPN is estimate of most probable number of nitrate reducers in mine spoil material based on five-tube assay.

^c The Bald Knob site was amended with lime and fertilizer, Osage with coal fly ash.

Source: Shirey and Sexstone, 1989.

Plant growth characteristics and N uptake patterns must also be carefully considered in land reclamation and forestry situations. In most cases the plants grown are perennials, not annuals, and hence have differing seasonal and long-term N uptake patterns. For example, a study of the use of inorganic fertilizers and poultry litters as N sources for managed pine forests in the southern United States showed that NO₃-N leaching losses could be considerable in early years because of the very low initial N uptake by young pine seedlings. Nitrate-N concentrations as high as 50 to 100 mg NO₃-N/L were measured below the rooting zone of pine seedlings. Delaying N applications until the trees were several years old and had better developed and deeper root systems was suggested as a BMP to reduce NO₃[–] leaching.

From a horticultural perspective, there has been increasing interest in the environmental implications of N management for greenhouses, nurseries, and turf. The soilless media used in many greenhouses and nurseries is not relied on to provide plant N requirements, but to serve as a physical growth medium. Instead, growers mainly use fertigation with high N concentration solutions, combined with intensive watering to remove salts from containers. This has raised questions about the impact of drainage waters from these facilities on groundwater and surface water quality. More efficient fertilization programs are being adopted in response to environmental concerns. Examples include use of slow-release fertilizers, “ebb-and-flow” fertigation systems where the nutrient solutions are recycled and reused, and onsite wastewater treatment systems. Similarly, improved N management programs for turf have been developed and promoted more intensively to homeowners and those involved in industrial or recreational turf management (e.g., golf courses, parks, athletic fields). Avoiding N losses from leaching or runoff is only part of the concern with turf operations. Overfertilization with N increases the frequency of cutting and the volume of grass clippings that must be recycled or disposed of in landfills. As many municipalities are no longer accepting yard wastes, the pressure to avoid the use of excess N, and to recycle N “on-site” through proper cutting schedules, mulching, or composting has increased.

8.3 NUTRIENT MANAGEMENT PRACTICES FOR PHOSPHORUS

Agriculture, in the broadest sense (farms, rangeland, managed forests, horticulture), has long been recognized as an important nonpoint source of P to surface waters. As described in Chapter 6, decades of research have shown a wide array of hydrologic processes (e.g., erosion,

interflow, overland flow, matrix flow, preferential flow) can transport P from land to water. As P controls eutrophication of most freshwaters, and even some estuarine systems, preventing nonpoint-source P pollution from agriculture is now an international environmental priority. In the United States, the importance of developing NMPs to control agricultural nonpoint P pollution became more obvious as municipalities and other point sources decreased P discharges to surface waters in the 1970s and 1980s, often under regulatory pressure. Although lowering point-source P loadings did result in improved water quality in some cases, accelerated eutrophication persists today as the most pervasive surface water impairment in the United States (U.S. EPA, 1996) and agriculture continues to be considered a major source of P to eutrophic water bodies (USGS, 1999).

Acting to reduce nonpoint P pollution of water bodies is much more complex than controlling point-source discharges. Successful implementation of BMPs to reduce nonpoint P pollution must address not only the technical aspects of P transport, but also the economic, social, and political considerations that affect farmers' willingness to adopt and maintain these practices. In the past decade, public concerns about agriculture's role in accelerated eutrophication have intensified and, in some countries, voluntary guidelines for P management are now being replaced by laws and regulations that mandate use of BMPs to mitigate P loss from agricultural operations to surface waters and groundwaters. The following sections provide the basic principles and specific BMPs now used to manage P for agricultural profitability and environmental protection.

8.3.1 General Principles of Efficient Phosphorus Management

Efforts to control nonpoint P pollution must be multidisciplinary in scope to be effective at minimizing the environmental impacts of soil P while sustaining agricultural productivity. Ideally, this begins, as discussed in Section 8.1, with strategic activities, such as the development of an NMP (or CNMP) and a balanced "farm-gate" P budget. Once an NMP is in place, site-specific, tactical BMPs for efficient P use can then be implemented. In general, as discussed in the following sections, (1) soil P should be maintained at a value that is adequate, but not excessive, for plant growth and economically optimum yields by proper management of inorganic and organic P sources, and (2) the transfer of dissolved and particulate P to surface waters by erosion, overland flow, and interflow, and to groundwaters by leaching should be minimized by use of soil and water conservation BMPs. An extensive information base and set of readily used BMPs are available to facilitate accomplishing these goals. Current soil P status, relative to optimum values required by most crops, can easily be assessed by soil testing and recent research has better defined soil P concentrations high enough to be of environmental concern. The properties and efficient application methods for inorganic and organic P sources are well-known, as are BMPs that should be implemented to reduce "edge of field" P losses (e.g., reduced tillage, buffer strips, grassed waterways, terraces). Controlling P movement beyond the field edge (e.g., in streams, ditches, and tiles that connect land and water) is more problematic, and fewer BMPs exist for this purpose. Building artificial wetlands between uplands and surface waters in need of protection is now being investigated as one option. One of the largest examples of this can be found in the Florida Everglades, where an 18,000-ha wetland has been built to trap P discharged to Everglades National Park from a large agricultural area just north of this important ecosystem.

8.3.2 Soil Testing for Phosphorus

Many types of agricultural operations, such as those producing agronomic crops, timber, vegetables, specialty crops (e.g., fruits, nuts, medicinal plants), commercial horticultural operations

(e.g., greenhouses, nurseries, turf farms), and recreational land uses (golf courses, athletic fields) need to develop and implement P management plans. Ensuring adequate soil P fertility is essential for economic plant production or sustained plant health in all these operations and many have implemented an array of BMPs to meet plant P requirements and protect water quality. However, in some situations, poor nutrient management has resulted in overuse of P fertilizers (inorganic and organic), causing the buildup of soil P to values where losses of dissolved P or P-enriched soils are now a concern for water quality. Thus, one of the most important aspects of efficient P management for any land use is a properly conducted soil testing program that monitors soils to prevent P deficiency and overfertilization with P.

The basic principles of soil testing are described in Chapter 4; here we apply them to soil P testing for agricultural and environmental purposes. The fundamental concept underlying soil P testing is illustrated in Figure 8.14, which depicts the well-known curvilinear relationship between soil test P, crop yield, and profitability. It clearly shows the need to apply P when soils are deficient, if optimum yields or plant performance is to be obtained, and also points to the potential for environmental problems to arise when soils are overfertilized with P.

In many areas of the world, as shown for the United States in Figure 8.15, widespread use of soil testing clearly indicates that P deficiencies are common and that P fertilization is needed to ensure economically optimum crop production. In these settings, the standard approach to soil testing should be followed. A soil sample is collected from the “topsoil” horizon (e.g., 0 to 20 cm for tilled cropland, 0 to 10 cm for grassland) and taken to a soil testing laboratory where it is then dried, ground, screened, and extracted with a chemical soil test that dissolves or desorbs an amount of P that is proportional to that which will be available for crop uptake during the time period of

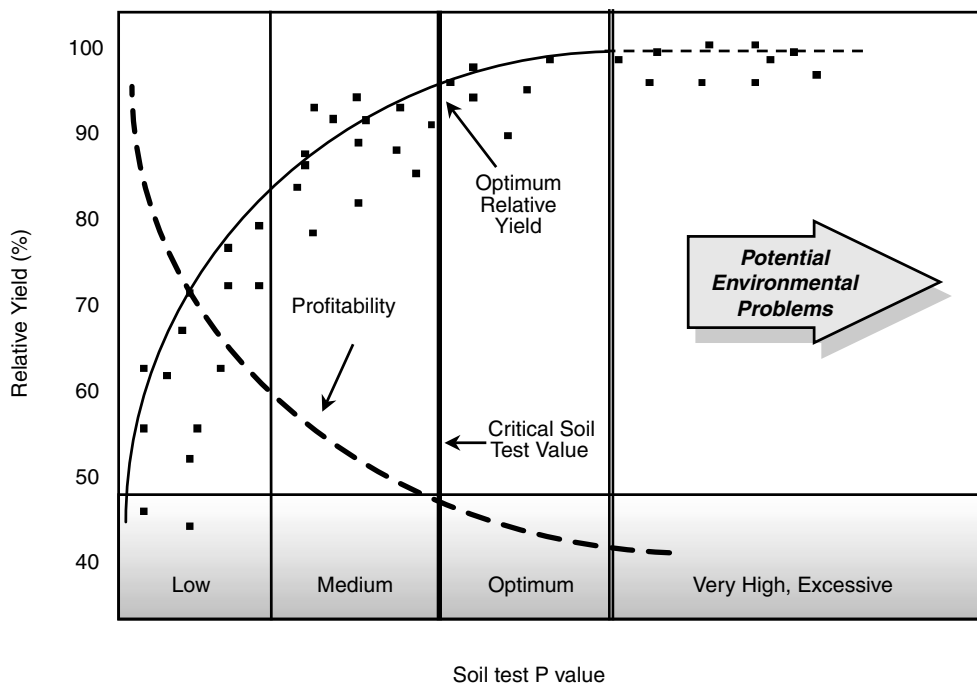


Figure 8.14 The relationships between soil test P, crop yield, profitability, and the potential for environmental problems when soil P increases to values above those required for economically optimum yields. Potential environmental problems include increased losses of dissolved P in overland flow and by leaching and erosion of soil particles that are highly enriched in forms of P that can become available in aquatic ecosystems, thereby enhancing eutrophication. Note that soils with optimum or lower soil test P values can also contribute to nonpoint P pollution if significant soil loss by erosion occurs. (From Sims, J. T., in *Handbook of Soil Science*, M. E. Sumner, Ed., CRC Press, Boca Raton, FL, D113–D153, 2000b.)

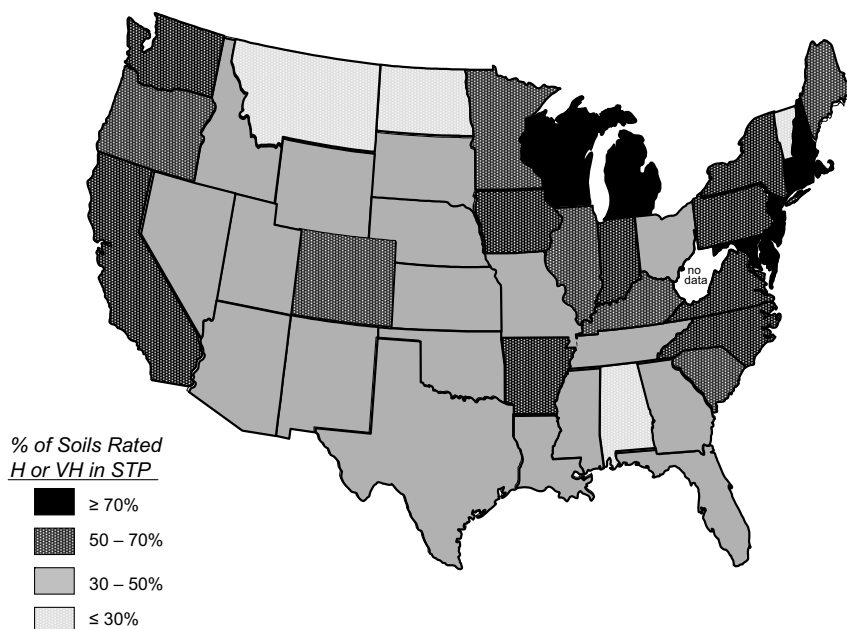


Figure 8.15 Soil test P (STP) summaries for the United States, for agricultural crop land only. H and VH = high and very high STP. (From Potash and Phosphate Institute, *Better Crops*, 86, 12–15, 2002. With permission.)

Table 8.11 Summary of Common Soil Testing Methods for Phosphorus

Soil Test	Extractant Composition	Comments, Critical Values ^a , and Ref.
AB-DTPA	1 M NH_4HCO_3 + 0.005 M DTPA – pH 7.5	Multinutrient extractant primarily used with alkaline soils; critical value: $\geq 8\text{mg/kg}$; Soltanpour and Schwab (1977)
Bray P_1	0.03 M NH_4F + 0.025 M HCl	Used only to extract P on acid soils with moderate CEC, critical value: $\geq 30\text{mg/kg}$; Bray and Kurtz (1945)
Mehlich 1	0.05 M HCl + 0.0125 M H_2SO_4	Multinutrient extractant used on acidic, low CEC soils; critical value: $\geq 25\text{mg/kg}$; Mehlich (1953)
Mehlich 3	0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA – pH 2.5	Multinutrient extractant suitable for wide range of soils; well correlated with Bray P_1 , Mehlich 1, and Olsen P; critical value: $\geq 30\text{--}50\text{mg/kg}$, depending on geographic location; Mehlich (1984)
Morgan	0.7 M $\text{NaC}_2\text{H}_3\text{O}_2$ + 0.54 M CH_3COOH – pH 4.8	Multinutrient extractant primarily used in the northeast United States for acid, low CEC soils; not suitable for calcareous soils; critical value: $\geq 4\text{--}6\text{mg/kg}$; Morgan (1941)
Modified Morgan	0.62 M NH_4OH + 1.25 M CH_3COOH – pH 4.8	
Olsen	0.5 M NaHCO_3 – pH 8.5	Originally developed as P extractant for alkaline soils in the western United States; now also used for acid and neutral soils; critical value: $\geq 10\text{mg/kg}$; Olsen et al. (1954)
Egner	P-CAL: 0.01 M Ca lactate + 0.02 M HCl P-AL: 0.10 M NH_4 lactate + HOAc – pH 3.75	Multinutrient extractant used in Europe and Scandinavia, but not in the United States; Egner et al. (1960)

^a Critical value is defined as the soil test concentration above which the soil test level is considered optimum for plant growth and responses to additions of the nutrient are unlikely to occur. Critical values cited in this table are approximate, can be affected by soil type and crop, and were obtained from several sources.

Source: Sims, 2000a. With permission.

interest (e.g., the crop's growing season). A number of different soil P tests are used throughout the world (Table 8.11). These soil tests were specifically developed and calibrated for the physiographic regions where they are used and for the crops that are grown in that region. The quantitative values for available P determined by a soil test are then compared with the "critical values" for soil test P (defined as the soil test value associated with economically optimum crop yields; above this value, economic responses to nutrient additions are unlikely). The critical value can vary numerically between soil P tests, but always has the same agronomic meaning. Soil test rating categories, such as "low," "medium," "high," "optimum," "very high," or "excessive" (Figure 8.14), are also defined and indicate the relative probability of an economic crop response to inputs of P when soil P is in each category. Recommendations for the amount of P to be applied are based on multisite, multiyear field studies with the crop of interest and may vary based on the P application method, as described below.

Example Problem 8.3

A soil sample is analyzed using the Mehlich 3 soil test, by extracting 2.5 g of soil with 25 mL of the Mehlich 3 solution. The P concentration in the extract is 8.4 mg/L. Does this soil need P fertilization for economically optimum crop yields?

$$\text{Mehlich 3 P (mg/kg)} = \frac{8.4 \text{ mg P}}{\text{L}} \times \frac{25 \text{ mL}}{2.5 \text{ g soil}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1000 \text{ g}}{\text{kg}} = \frac{84 \text{ mg P}}{\text{kg soil}}$$

The soil test is above the critical level for Mehlich 3 P (30 to 50 mg/kg); no fertilizer P is needed.

In contrast to the use of soil testing to guide correction of P deficiencies, the goal of "environmental P testing" is to help identify soils with a high potential for nonpoint pollution of surface waters or shallow groundwaters. This is necessary because past and ongoing applications of P in fertilizers and/or organic by-products, either without the use of soil P testing or despite test results that clearly indicate no additional P was needed, have overfertilized soils to the point of environmental concern. Once soils are overfertilized with P, it may take many years before an economic response to P fertilization will occur (with the possible exception of P in "starter" fertilizers; see Section 8.3.3). An example of the long "draw-down" period required for high P soils is given in Figure 8.16, where about 15 years were needed to reduce soil test P (Mehlich 1) from ~100 mg P/kg to a yield-limiting level for maize (~20 to 25 mg P/kg).

Given the long-term nature of potential environmental problems with high P soils, use of existing agronomic soil P tests, or new soil test methods, to identify soils with a high risk of P transfer to water has received intense research interest for more than a decade. Agronomic soil P tests have long been known to be well correlated with other measures of soil P that suggest increased risks of P loss, such as the equilibrium P concentration in the soil solution (EPC_0 ; see Chapter 6) and algal-available P (Figure 8.17). More recently, studies of the relationships between agronomic soil test P and dissolved P concentrations in overland flow or leachate provided direct evidence for increased risks of P loss from overfertilized soils (Figure 8.18). In some cases, this relationship was near-linear, while in others there appeared to be a "change point" above which there was a more rapid increase in P concentrations in runoff or leachate with increases in soil test P. Research has also shown that maintaining soil test P in the optimum range for plant growth minimizes dissolved P losses (Figure 8.18). When combined with information on soil erosion, soil test P can also be used to assess the risk of particulate P loss to water, as is done by risk assessment tools such as the P Site Index (see Chapter 6).

"Environmental soil P testing" is not confined to the use of agronomic soil P tests. It may mean the use of completely different methods for soil sampling, analysis, and interpretation than

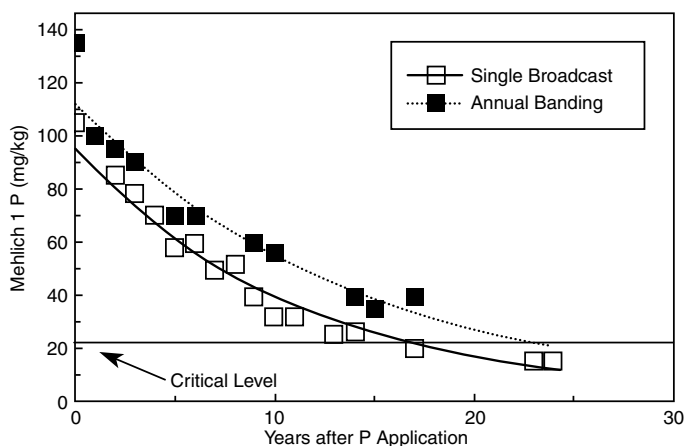


Figure 8.16 Decrease in soil test (Mehlich 1, 0.05 M HCl + 0.125 M H₂SO₄) extractable P in a Portsmouth soil cropped to a corn–soybean rotation for 26 years. Initial soil test P values ($T = 0$ years) resulted from a single broadcast application of 324 kg P/ha or eight annual banded applications of P at 60 kg P/ha. (From McCollum, R. E., *Agron. J.*, 83, 77–85, 1991. With permission.)

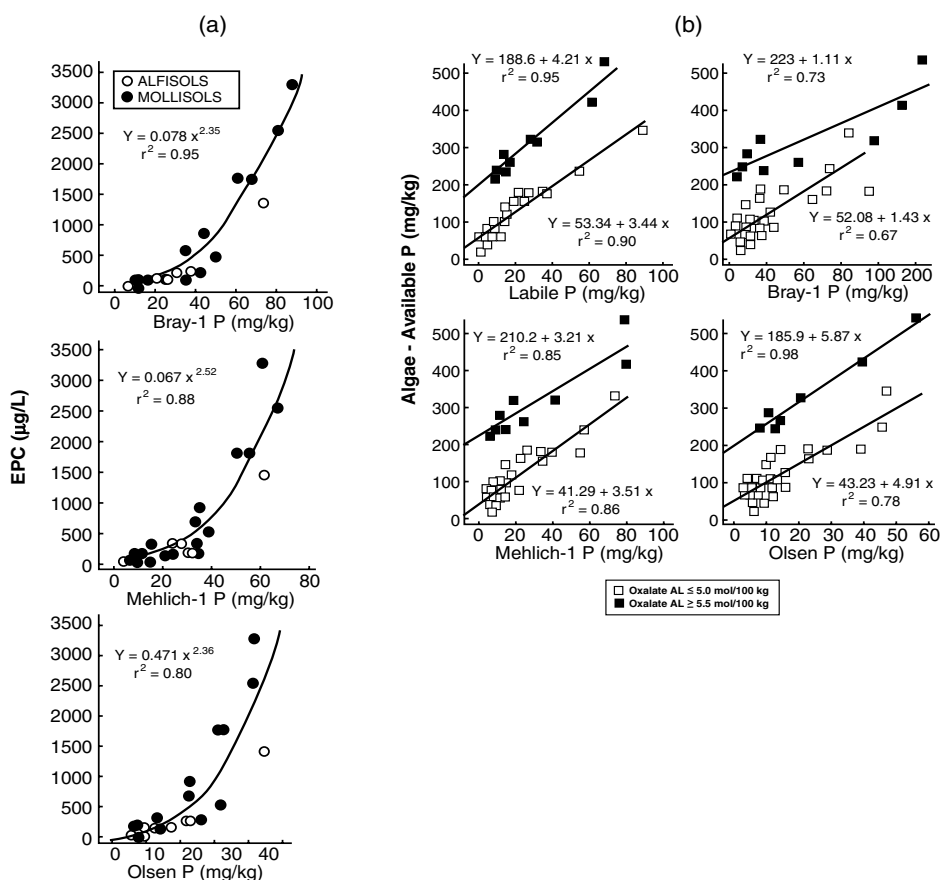


Figure 8.17 Examples of the use of routine soil tests (Olsen P, Mehlich-1 P, Bray-1 P) to predict parameters useful for the assessment of the environmental impact of soil P: (a) equilibrium P concentration at zero sorption (EPC₀) and (b) algal-available P. (From Wolf, A. M. et al., *J. Environ. Qual.*, 14, 341–348, 1985. With permission.)

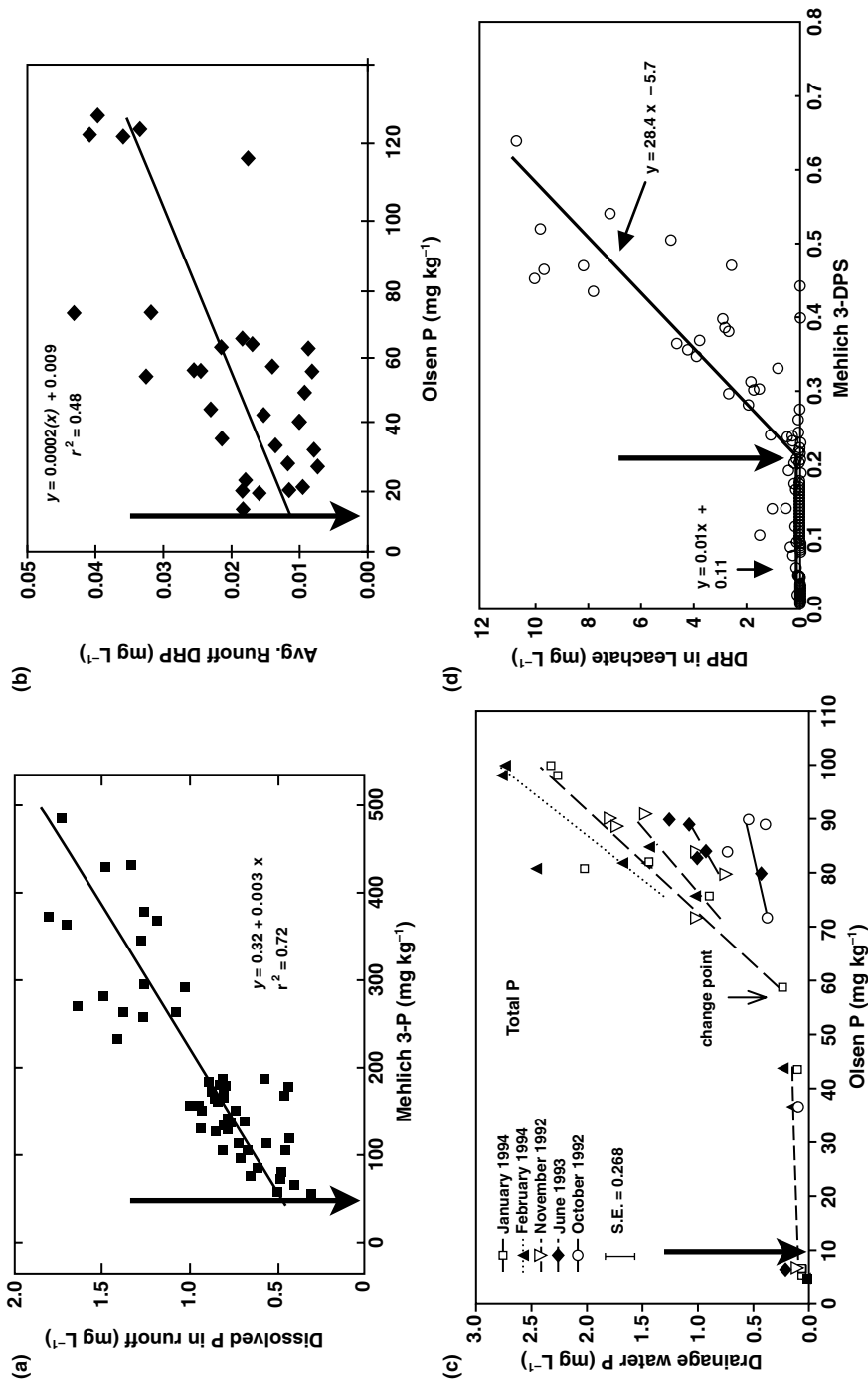


Figure 8.18

Relationship between agronomic soil test P and concentrations. (a) Dissolved reactive P in runoff from fescue pasture. (From Pote, D. H. et al., *Soil Sci. Soc. Am. J.*, 60, 855–859, 1996. With permission.) (b) Furrow irrigation runoff in the western United States (From Westernman, D. T. et al., *J. Environ. Qual.*, 30, 1009–1015, 2001. With permission.) (c) Total P in drainage water from plots at the Broadbalk experiment in Rothamsted, U.K. (From Heckrath, G. et al., *J. Environ. Qual.*, 24, 904–910, 1995. With permission.) (d) Soil P saturation measured by the Mehlich 3 soil test and dissolved reactive P in leachate from undisturbed soil columns collected from five Delaware soil series. (From Maguire, R. O. and J. T. Sims, *Soil Sci. Soc. Am. J.*, 66, 2033–2039, 2002. With permission.) Arrows indicate typical soil test critical values for these soil P tests.

those done for agricultural purposes. Or, it may mean that an environmental or regulatory interpretation is now being applied to results of an agronomic soil P test, such as establishing an upper limit for soil test P beyond which no further P additions can be made. Changes in soil sample collection may include sampling to a shallower depth (0 to 5 cm) if overland flow is of greatest concern or to the depth of the mean high water table (e.g., 50 to 150 cm) if P leaching and subsurface flow is the main pathway for P loss. Different analytical methods may be used, such as assessment of the degree of soil P “saturation” (DPS), water-soluble P, easily desorbed P, “algal-available” P, and quick tests for P sorption capacity (see Figure 8.17). For example, a DPS_{ox} method based on acid ammonium oxalate extraction of P, Al, and Fe was developed in the Netherlands to identify soils where P leaching to shallow groundwaters is a risk (Figure 8.19a).

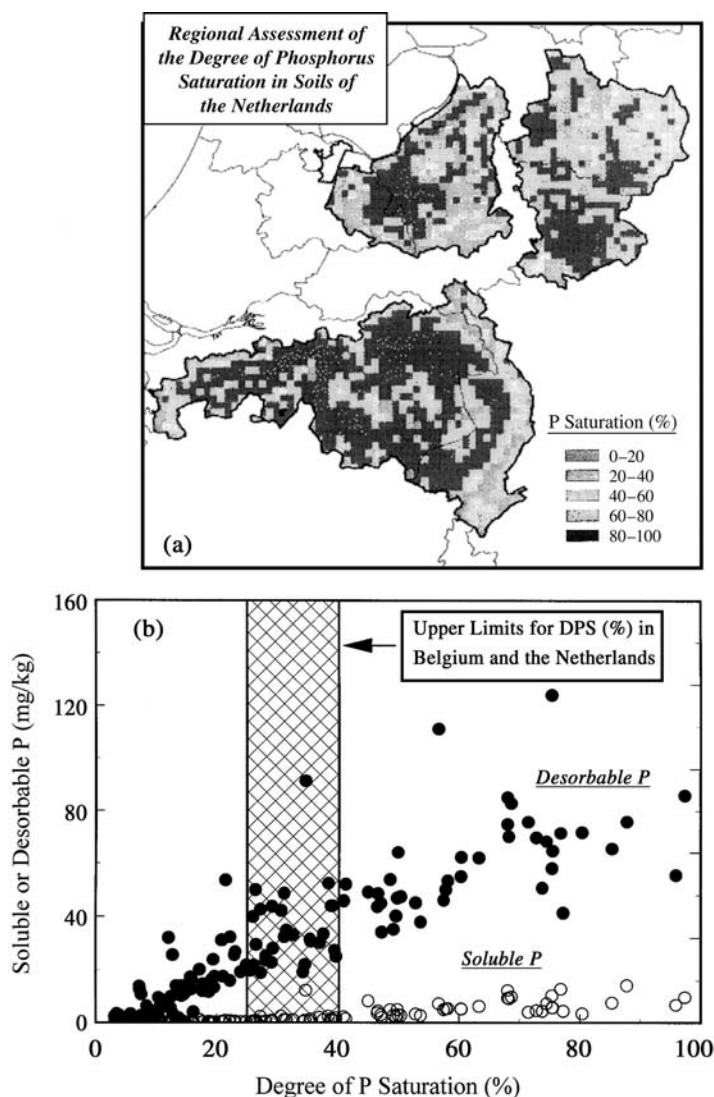


Figure 8.19 (a) Regional assessment of the degree of P saturation in the southern Netherlands. Areas with darker shadings are progressively more saturated with P in the soil profile to the depth of the mean high water table. (From Breeuswma, A. et al., in *Animal Waste and Land-Water Interface*, K. Steele, Ed., Lewis Publishers, Boca Raton, FL, 1995.) (b) Relationship between the degree of P saturation in 85 Delaware soils and easily desorbable and soluble P, and a comparison to upper limits for DPS in Belgium and the Netherlands. (Adapted from Pautler and Sims, 2000.)

Oxalate extractable P (P_{ox}) represents the amount of P currently sorbed by the soil and oxalate Al and Fe (Al_{ox} , Fe_{ox}) are proportional to the P sorption capacity of noncalcareous soils. The molar ratio of P_{ox} to $[\alpha(Al_{ox} + Fe_{ox})]$ is thus an indication of soil P saturation (where α is a parameter used to convert $(Al_{ox} + Fe_{ox})$ to estimated soil P sorption capacity and typically ranges from 0.4 to 0.6). Upper limits for DPS_{ox} of 25 to 40% have been proposed. Research has found increases in water-soluble and desorbable P in soils above these DPS_{ox} values, suggesting a greater risk of P loss to surface waters and shallow groundwaters from P-saturated soils (Figure 8.19b). Recently, research showed that DPS measured by the Mehlich 3 (M3) soil test was well correlated with DPS_{ox} and also with P concentrations in leachate and overland flow (Figure 8.18d). The Mehlich 3 soil P test is widely used in the United States and Canada, so soil testing laboratories could report a soil P fertility assessment (M3-P) and soil P saturation (M3-DPS) using one soil extraction.

Example Problem 8.4

A field near an important lake in a watershed is sampled to determine DPS in the topsoil because of concerns about high concentrations of dissolved P in runoff. The sample is extracted with acid ammonium oxalate (soil:solution 1:40) and found to contain 11.6 mg P/L, 29.8 mg Al/L, and 10.7 mg Fe/L. Calculate DPS for this soil and, using Figure 8.19b, estimate the concentration of easily desorbable P in this soil (assume $\alpha = 0.5$). Do your results suggest this field needs improved P management to reduce dissolved P losses to the lake?

$$DPS_{ox} (\%) = \frac{P_{ox} \text{ (mmol/kg)}}{\alpha(Al_{ox} + Fe_{ox} \text{ (mmol/kg)})} \times 100$$

First, convert P_{ox} , Al_{ox} , and Fe_{ox} in the soil to units of mmol/kg:

$$P_{ox} = \frac{11.6 \text{ mg P}}{\text{L}} \times \frac{1 \text{ mmol P}}{30.97 \text{ mg}} \times 40 = \frac{15 \text{ mmol P}}{\text{kg}}$$

$$Al_{ox} = \frac{29.8 \text{ mg Al}}{\text{L}} \times \frac{1 \text{ mmol}}{26.98 \text{ mg}} \times 40 = \frac{44.2 \text{ mmol Al}}{\text{kg}}$$

$$Fe_{ox} = \frac{10.7 \text{ mg Fe}}{\text{L}} \times \frac{1 \text{ mmol}}{55.85 \text{ mg}} \times 40 = \frac{7.7 \text{ mmol}}{\text{kg}}$$

Then calculate DPS_{ox} :

$$DPS_{ox} = \frac{15 \text{ mmol P/kg}}{0.5(44.2 \text{ mmol Al/kg} + 7.7 \text{ mmol Fe/kg})} \times 100 = 58\%$$

The estimated concentration of easily desorbable P in this soil is approximately 42 mg/kg; more intensive P management should be considered for this field.

With the possible exception of the M3-DPS test, environmental P tests would probably not be conducted on every sample submitted as part of an NMP. Instead, they would be part of a more intensive testing procedure used when agronomic soil test P values were considered high enough to warrant further investigation. Ideally, environmental soil P tests would not be used

alone, but as a component of a more holistic risk assessment process, such as the P Site Index (Chapter 6) that integrates soil P with P transport and management practices to characterize the potential for P loss at a site. For example, the states of Delaware and Maryland in the United States require that a P Site Index be conducted for fields with an agronomic soil test P (Mehlich 3) value >150 mg P/kg.

8.3.3 Phosphorus Sources and Application Methods

Many soils, because of P-deficient parent material, low organic matter, or intensive cropping, do not have adequate plant-available P and must be amended with fertilizers or by-products to achieve the desired level of plant growth. Once a P deficiency has been identified by soil P testing, the next step is use of BMPs that optimize P fertilization efficiency. This requires identifying the most cost-effective P source, P rate, and best combination of application method and timing to maximize P uptake by plants and minimize the potential for loss of applied P. The basic properties of inorganic and organic P sources are discussed in Chapter 6. This section focuses on BMPs related to the methods used to apply fertilizer or by-product P sources to soils.

The most common techniques used to apply commercial fertilizer P are some types of broadcasting (uniform application over the area to be fertilized) or banding (placing P in a concentrated band in close proximity to the seed or growing crop). Broadcasting can be done before planting, with or without incorporation by tillage, or can be “top-dressed” to a growing crop, such as a pasture or forage. Banding of P fertilizers is most commonly done at planting by placing “starter” fertilizers near the seed (e.g., 5 cm deep and 5 cm to the side of the seed). Lower P rates are usually recommended when fertilizer P is banded than when it is broadcast over the soil surface and tilled into the soil. Banding reduces P sorption by exposing less of the added fertilizer P to the soil in the crop rooting zone. It also increases P uptake by enhancing diffusion of P because the distance that P must move from where the fertilizer band is placed in the soil to plant roots is greatly reduced and the concentration gradient between the P source (fertilizer band) and P sink (plant roots) is much higher. Starter fertilizers often produce more vigorous early plant growth, greater resistance to early season pest and weather stresses, and occasionally, but not always, increased crop yields (Figure 8.20). Responses to starter

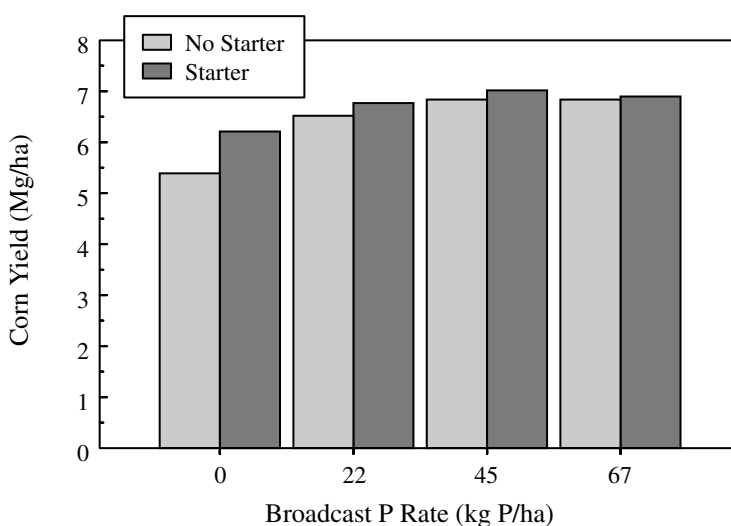


Figure 8.20 The effect of starter fertilizer on corn yield. Results of a 20-year study in Iowa comparing the use of starter P applied with differing rates of broadcast P at 3-year intervals. (From Young, R. D. et al., in *Fertilizer Technology and Use*, O. P. Engelstead, Ed., American Society of Agronomy, Madison, WI., 1985. With permission.)

fertilizers can even occur in well-fertilized soils, particularly cold and wet soils. These responses can be explained by lower rates of mineralization of soil organic P, slower diffusion of soluble P through soil pores to roots, and reduced growth of plant roots early in the growing season when soil temperatures are cooler. As soils warm, microbial and chemical reactions are more rapid, root systems expand, and the P supply to plant roots increases to acceptable levels. Because of this, it is rather common to see early-season vegetative responses to starter fertilizers in high P soils that are not always followed by increases in crop yields. Fewer options are available to apply organic P sources, mainly because they are bulky, low-analysis materials that require high rates to meet crop P needs and can also be difficult to handle and apply uniformly. Most by-product P sources are applied by broadcasting over the surface, with or without tillage, although some liquid manures and biosolids can be injected into the soil in a manner similar to banding inorganic fertilizers.

In general, the most efficient P application method for both agricultural and environmental purposes is to apply P sources as close as possible to the time of crop P uptake and to incorporate them into soils by tillage or injection. Applying P far in advance of cropping increases the chance for P loss, particularly if fertilizers or manures are applied on soil surfaces and rainfall events occur shortly after application (Figure 8.21). Incorporation prevents the direct interaction of overland flow with fertilizers and manures, reducing P loss by this pathway. Incorporation also mixes P into the plow layer (0 to 20 cm) thus preventing buildup of P to very high concentrations in the upper few cm of soil that are most likely to interact with surface runoff, as can occur when P is used in no-tillage agriculture (see Figure 6.18). The potential reductions in total and dissolved P losses in runoff due to incorporating fertilizer P (diammonium phosphate, DAP) and three types of manures (dairy, poultry, swine) are clearly shown in Figure 8.22.

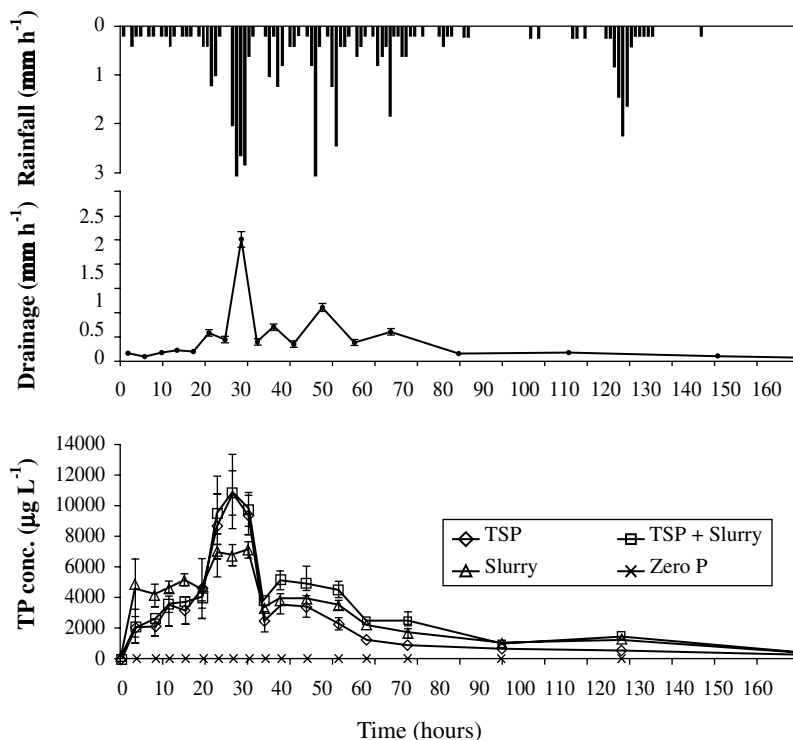


Figure 8.21 Relationship between rainfall, runoff water discharge, and total P concentrations in overland flow from a perennial ryegrass pasture in southwest England shortly after application of fertilizer (triple superphosphate, TSP) or dairy manure slurry. (From Preedy, N. et al., *J. Environ. Qual.*, 30, 2105–2110, 2001. With permission.)

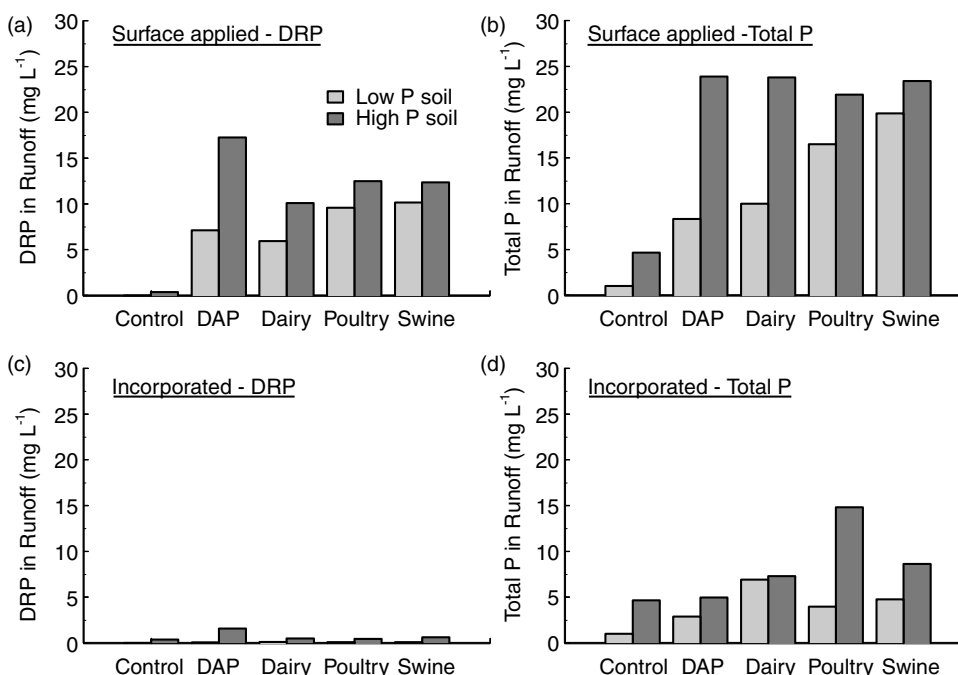


Figure 8.22 Effect of surface applications (a, b) or incorporation (c, d) of fertilizer P (diammonium phosphate, DAP) or manures on total and dissolved reactive P (DRP) concentration in surface runoff. (From Kleinman, P. J. A. et al., *J. Environ. Qual.*, 31, 2026–2033, 2002. With permission.)

Incorporation of P sources is not a panacea, however. In some settings, such as grasslands, or highly erodible soils where conservation tillage must be used, it may not even be possible to incorporate P sources. Most incorporation methods also leave bare soil exposed to rainfall, snowmelt, and wind, increasing the potential for P loss by erosion. Preventing erosion, which has many other environmental impacts beyond P transfer to water, is one reason for the long interest in conservation tillage (e.g., no-till, chisel plowing, ridge-till). Conservation tillage is particularly difficult to reconcile with manure and biosolids applications where equipment to incorporate these materials without tillage has not been readily available and also increases the time and costs of application. Complicating the issue further is the fact that P applications (manures and fertilizers) may also be done after the growing season, when farmers have more time available, or when frozen ground makes it easier to move equipment through fields. Fall, winter, and early spring surface applications of inorganic or organic sources of P enhance the likelihood of P loss to water during the late winter or early spring, typically when the greatest percentage of annual rainfall and snowmelt occurs. Reconciling the need to incorporate P sources in a timely manner, while at the same time minimizing erosion and avoiding damage to soils and crops, is an ongoing dilemma. Some solutions do exist, such as using specialized equipment to inject organic P sources into pastures or no-till soils, which can also reduce odors and ammonia emissions. Injection will leave a significant amount of crop residue in place and does not injure crops. As discussed next, incorporation can be combined with more extensive use of soil conservation BMPs designed to reduce soil erosion and particulate P loss.

8.3.4 Soil and Water Conservation Practices for Phosphorus

Soil and water conservation practices designed to reduce the impact of P on water quality have traditionally focused on preventing soil loss by erosion because this usually is the dominant process

by which P is transferred from land to water. Controlling soil erosion is also needed to prevent long-term degradation of soil quality. Many erosion control practices have been developed, such as conservation tillage, contour plowing, terracing, buffer strips, and grassed waterways. Key BMPs for soil and water conservation are summarized in Table 8.12. Detailed descriptions of the principles and design for most widely used soil conservation BMPs are found in the USDA NRCS Field Office Technical Guide (<http://www.nrcs.usda.gov/technical/efotg/>).

Many studies, such as those highlighted in Table 8.13, have shown the value of BMPs such as reduced tillage practices (chisel plow or no-till vs. conventional), crop residue strips, buffer zones, and grassed waterways, in trapping sediment-bound P. These studies also illustrate the importance of considering all aspects of erosion/runoff control practices to maximize the overall efficiency of a management system. For example, as shown in Table 8.13, chisel plowing may be just as effective in controlling erosion and runoff as complete no-tillage in certain soils. Chisel plowing also improves crop yield and nutrient uptake by breaking compaction zones and improving root growth; it also provides a method to at least partially incorporate organic P sources. Narrower crop residue strips may be equally effective as wider strips in reducing P loss, if adequate soil cover is present. Grass buffer strips may reduce sediment load by 75%, but may need to be wider or combined with forested buffers to achieve similar reductions in P loss. Multiple cutting practices for grassed waterways increased the efficiency of P removal in an overland flow wastewater renovation system. However, equipment damage to the grassed waterway caused by extra cuttings produced ruts and channels that increased runoff. Each example in Table 8.13 clearly shows the need to reduce P loss must be balanced with other aspects of the system (e.g., crop growth in severely compacted soils, loss of cropland by conversion to filter strips, sustainability of grassed waterway) to optimize overall BMP efficiency.

Preventing P loss to water in settings where the movement of dissolved P by overland flow or leaching is a major concern is more complicated. The BMPs designed to control P loss by erosion by physically preventing soil movement are often ineffective at removing dissolved P from surface runoff and are not intended to reduce P concentrations in subsurface runoff or leachate. In general, the best management strategy to prevent dissolved P losses is to avoid, or discontinue, unnecessary applications of P that result in P-saturated soils. If always done, it is unlikely that dissolved P losses will be a problem; if P applications are discontinued in settings where soils are already P saturated, with time, removal of P in crop harvest will eventually deplete soil P to values where dissolved P concentrations in runoff are not a water quality threat. However, as shown earlier in Figure 8.16, it may be years before this occurs for P-saturated soils.

The value of altering the properties of P sources to reduce dissolved P losses in runoff and leachate from soils amended with organic P sources was discussed earlier (see Figure 6.13). Other options now being considered include amending soils with by-products that have high P sorption capacities; constructing wetlands between uplands and surface waters where P uptake by wetlands vegetation and P sorption by sediments will reduce dissolved P concentrations; and deep plowing to mix high P topsoils with low P subsoils resulting in a lower soluble P concentration in the mixed soils. Results from research investigating these options is shown in Table 8.14. Drinking water treatment residuals (WTR: an Al/Fe-based by-product of the treatment of drinking waters to remove suspended inorganic solids, organics, and color) can precipitate or sorb soluble P and increase soil P sorption capacity when added to soils in buffer strips or grassed waterways. Although this practice may decrease soluble P and increase the capacity of the amended soil to remove P from runoff waters, it must be balanced against the need to maintain an adequate P supply for vegetation in these areas. Plowing high P topsoils to reduce their P concentration by mixing them with low P subsoils that may also have higher P sorption capacities can decrease dissolved P losses in runoff. However, plowing will initially increase particulate P losses; therefore, this practice must be combined with more intensive use of erosion

Table 8.12 Overview of Soil and Water Conservation Practices That Can Be Used To Reduce Phosphorus Losses in Erosion and Runoff

Practice	Soil and Water Conservation Benefits
Conservation tillage	Conservation tillage is a tillage system that leaves at least 30% of the soil surface covered by plant residue after planting to reduce erosion and runoff. A variety of tillage systems fall under conservation tillage, including stubble mulch tillage, minimum tillage, reduced tillage, and no-till. Conservation tillage may also make the soil surface porous, cloddy, rough, or ridged, which increases infiltration and reduces runoff.
Contour cultivation	Contour cultivation follows the contour lines of sloping fields. Contour ridges produced by tillage and planting form barriers that slow or stop downhill water movement and decrease runoff and erosion.
Deep chiseling	Deep chiseling or deep plowing can break up pans at plow depth or slightly below to increase water infiltration and reduce runoff and erosion.
Vegetative soil cover	Rainfall breaks up soil aggregates, allowing soil particles to move with runoff, and compacts and puddles the soil surface, decreasing water infiltration and increasing runoff volume. Crops can intercept up to 45% of rainfall, dissipating raindrop energy and reducing the ability of the rainfall to initiate runoff and erosion. After planting cash crops, cover crops, or green manures, it is essential to achieve canopy closure quickly to minimize soil exposure. Adequate soil fertility, optimum seed bed preparation and planting conditions, such as soil moisture and temperature, and pest control will promote seed germination, plant growth, and canopy closure. Plant populations, row spacing, and plant spacing that achieve equidistant plant separation also maximize soil coverage.
Crop rotation	Crop rotation enables a grower to plant a new crop soon after the preceding crop is harvested and minimize soil exposure time. Rotations can also help break insect, disease, or weed cycles that could impede plant growth, increase time to canopy closure, and reduce plant cover.
Companion crops	With companion crops such as small grain/forage crops the small grain starts first and provides quick plant cover. Harvesting the small grain leaves residue and the growing forage crop to protect the soil. Later, the forage crop provides excellent plant cover.
Cover crops	Cover crops grown during cold or dry seasons unfavorable for cash crops protect the soil by filling time and space gaps when cash crops leave the soil bare. Cover crops should germinate easily, grow quickly, provide sufficient plant cover, and be hardy against weather and pests.
Green manures	Green manures act as cover crops and when plowed under can add nutrients to soil to increase fertility for succeeding crop growth and soil organic matter content to promote the soil structure, permeability, and aeration needed to maximize rainfall infiltration and minimize runoff and erosion.
Crop residues	Crop residues act as mulch to increase soil coverage. Although plowing the residue under decreases soil coverage, it can promote residue decomposition and benefits similar to green manures.
Strip cropping	Strip cropping divides fields into long, narrow segments that help control runoff and erosion while growing crops in rotation. More heavily vegetated strips slow runoff and catch soil eroded from more exposed strips. Strips planted on the contour of slopes (contour strip cropping) are especially effective in controlling runoff and erosion.
Terraces	Terraces divide a slope so that runoff water is intercepted and carried to a protective outlet. Terraces help to decrease erosion by shortening slope length, slowing runoff velocity, and trapping sediments.
Vegetated waterways	Runoff water concentrates in waterways that when bare or unstable are extremely erodible. Vegetated waterways are natural or constructed channels that, when properly established and maintained, transport runoff water at a nonerosive velocity from fields, prevent gully formation, and greatly decrease erosion.
Buffer strips	Vegetated buffer strips keep soil from being carried into streams, ponds, or drainage ditches that need protection. Buffer strips primarily control water pollution. Erosion reduction may only be secondary.

Sources: Sims and Vadas (1997); Troeh et al. (1991).

Table 8.13 Examples of Some Methods Used to Control Particulate Phosphorus Losses

Tillage Practices for Corn^a (total P loss in runoff, mg/m²)						
Tillage Method	1980	1981		1982	1983	
	September	June	July	October	June	July
Conventional	133	8	230	220	175	22
Chisel plow	21	<1	20	37	67	11
No-till	39	<1	20	24	21	5

Cornstalk Residue Management^b				
Available P (g/h/m of width)				
Strip Width (m)	% Cover	Entering	Leaving	Reduction in P Loss (%)
1.8	27	0.98	0.77	21
1.8	50	1.39	0.70	50
2.7	50	2.63	0.48	82
4.6	50	1.80	0.51	72

Buffer Strip Width and Type Affect P Loss in Runoff^c							
Buffer Width (m)	Buffer Type	Sediment			P		
		Input (mg L⁻¹)	Output (mg L⁻¹)	Reduction (%)	Input (mg L⁻¹)	Output (mg L⁻¹)	Reduction (%)
4.6	Grass	7284	2841	61	11.3	8.1	29
9.2	Grass	7284	1582	75	11.3	8.6	24
19.0	Forest	6480	661	90	5.0	1.5	70
23.6	Grass/ Forest	7284	290	96	11.3	2.4	79
28.2	Grass/ Forest	7284	188	97	11.3	2.6	77

Wastewater Renovation by a Reed Canarygrass Waterway^d			
P Removal Efficiency from Wastewater (%)			
Cover Crop Management	Dissolved P		Total P
Multiple cuttings, harvest crop residue	32		70
Multiple cuttings, leave crop residue	20		62
Cut once, leave crop residue	4		50

^aAndraski et al., 1985.^bAlberts et al., 1981.^cChesapeake Bay Program, 1995.^dPayer and Weil, 1987.

control measures. As shown in Table 8.14, dissolved P loss in overland flow from a high P soil used for no-till corn production decreased from 364 to 10 g/ha after chisel plowing and subsequent establishment of an orchardgrass crop. Particulate P initially increased from 84 to 543 g/ha, but then decreased to 41 g/ha as the orchardgrass became established and deterred soil erosion.

Table 8.14 Examples of Some Methods Used to Control Dissolved Phosphorus Losses

Use of By-Products to Decrease Soluble P and Mehlich 3 P^a (mg/kg)				
	Dickson Silt Loam		Keokuk Very Fine Sandy Loam	
	Soluble P	STP	Soluble P	STP
Control (no by-product)	14	550	4	300
Water treatment residual #1	2	425	1	225
Water treatment residual #2	1	375	1	220
Cement kiln dust	4	375	2	180
Bauxite red mud	4	480	3	230

Use of Chisel Plowing to Decrease Dissolved Reactive P (DRP) Losses^b				
Time (weeks)	Sediment (kg/ha⁻¹)	DRP (g/ha)	Particulate P (g/ha⁻¹)	Total P (g/ha)
<i>Unplowed High P Soil</i>				
5	26	325	39	354
10	28	378	70	448
20	48	448	64	512
30	50	288	63	351
<i>Chisel Plowed High P Soil</i>				
Before Plowing				
0	25	364	68	432
3	22	448	63	511
8	34	419	84	502
After Plowing and Planting Orchardgrass				
9	559	243	543	786
10	318	184	478	662
12	336	205	328	533
16	190	118	274	391
24	74	30	167	197
28	53	15	153	168
52	16	14	30	44
60	20	10	41	51

^a Peters and Basta, 1996.^b Sharpley, (2003).

Environmental Quality Issues/Events

Improving Agricultural Nutrient Management in the Chesapeake Bay Watershed

Background: The Chesapeake Bay is one of the most important estuarine ecosystems in the world. In addition to its priceless value as a natural ecosystem, the bay is vital to the economies of the surrounding states, which rely on its waters for fishing, recreation, and tourism. Unfortunately, years of point- and nonpoint-source pollution by nutrients, sediments, and toxics have degraded water quality in the bay to the point that it is now regarded as seriously polluted. In 2003, the Chesapeake Bay Foundation (CBF) rated the health of the bay as “27 out of 100,” using an index derived from parameters related to habitat quality and quantity, water pollution, and the status of fish and shellfish populations. The CBF commented that the coordinated efforts of public agencies, private groups, and individuals had stabilized the decline in the health of the bay, primarily by reducing nutrient and sediment loads. These reductions led to increases in submerged aquatic vegetation and some fish populations. However, the CBF cautioned that more intensive efforts were needed to meet their bay health goals of 40 by 2010 and 70 by 2050.

A key factor in regional efforts to restore the bay was the 1983 establishment of the Chesapeake Bay Program (CBP) to support research and education efforts and regulatory programs in the watershed. Partners in the CBP are the EPA, state governments (Maryland, Pennsylvania, Virginia), the District of Columbia, and many advisory groups. Although it is unlikely that the bay will ever return to the pristine status of the 1600s, a health index of 70 is regarded as attainable. Should this occur, improvements in fish and shellfish populations, submerged aquatic vegetation, and water quality will produce a more resilient, healthier Chesapeake Bay ecosystem.

Nutrient Pollution of the Chesapeake Bay: The Chesapeake Bay drains a 170,000-km² watershed in six states (Delaware, Maryland, New York, Pennsylvania, Virginia, West Virginia) and the District of Columbia (Figure 8.23). Land use in the watershed is diverse. About 60% of the watershed is forested, 30% is in agriculture (cropland and pastures), and 10% is urban or suburban land. Agriculture has been identified as a major nonpoint source of nutrients to the bay; some studies suggest that >50% of the P and >33% of the N entering the bay come from agriculture. In some areas of the watershed these values are much higher. For example, on Maryland's lower Eastern Shore (site of a highly concentrated poultry industry) ~70% of the N and 82% of the P inputs are from agriculture.

The CBP recognized from its inception in 1983 that reducing nutrient inputs to the bay was essential to its restoration goals. The initial target was a 40% reduction in the amount of N and P entering the bay by the year 2000. Indications today are that, while substantial progress has been made toward this goal, continued and more intensive efforts will be needed to reduce nutrient inputs to desired levels. Indeed, in 2003, new nutrient reduction targets were agreed upon by regional bay restoration leaders. The new goals call for a reduction of N and P entering the bay, from point and nonpoint sources, from current values of 130 and 8.7 million kg/year to 80 and 5.8 million kg/year. In comparison, N and P loadings in 1985, when coordinated efforts to reduce N and P entering the bay began, were 153 and 12.2 million kg/year, respectively. Some important steps taken to reduce nutrient loading have included banning P-based detergents in some states (Maryland, Virginia) and the District of Columbia, more efficient nutrient removal by wastewater treatment plants, expanded efforts to restore forested riparian buffers, and a concerted effort to develop and implement BMPs for agriculture.

Innovations in Agricultural Nutrient Management in the Chesapeake Bay Watershed: The issue of agricultural nonpoint nutrient pollution is one of the most problematic faced by those involved in restoring the health of the bay. Groundwaters discharging into the bay are elevated in NO₃-N, much of which comes from decades of widespread use of fertilizers and manures in crop production. The well-drained nature of many agricultural soils in the watershed and plentiful rainfall in the region have always made it difficult to prevent NO₃-N leaching. Extensive reviews of soil P status in the watershed in the 1990s found that ~70% of soil samples from agricultural cropland were “optimum” or “excessive” in P, often due to long-term overapplication of manures or fertilizers, raising concerns about erosion of P-rich soils and dissolved P losses by runoff and leaching. Animal agriculture is geographically concentrated in the bay watershed (Figure 8.24), resulting in localized manure excesses and nutrient surpluses. Municipalities have similar surpluses of biosolids. Few, if any, options to land application of organic nutrient sources are available; hence, these materials are often applied to soils that do not require nutrients for optimum crop yields.

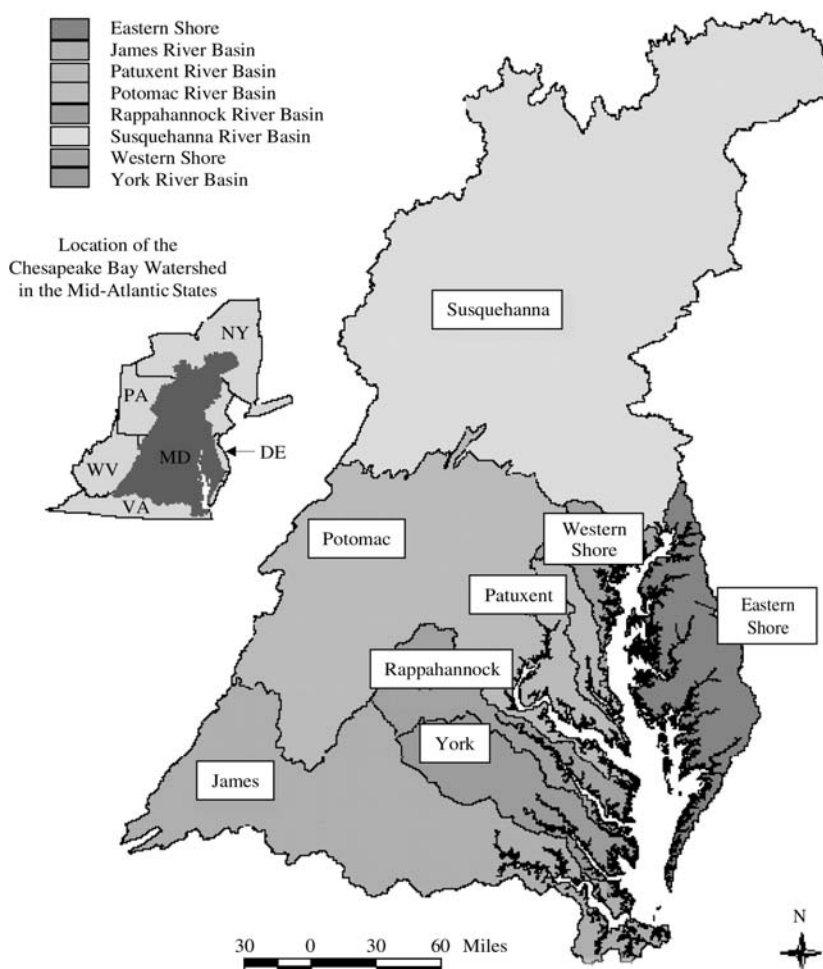


Figure 8.23 Location of the Chesapeake Bay Watershed in the eastern United States, indicating the location of the six states (DE: Delaware; MD: Maryland; NY: New York; PA: Pennsylvania; VA: Virginia; WV: West Virginia) and eight major basins in the watershed. (From Chesapeake Bay Program, 2000.)

Given these challenges, what steps are being taken today to improve agricultural nutrient management in the Chesapeake Bay Watershed?

Nutrient Management Plans: As noted earlier, NMPs are now required by law in four bay states (Delaware, Maryland, Pennsylvania, Virginia) and CNMPs are required by USDA in the Code 590 standard and by the EPA in the new CAFO regulations. The hope is that, as widespread implementation of these laws and regulations occurs, the value of NMPs and CNMPs at reducing N and P exports to the bay will become apparent. These plans address not only field-scale nutrient recommendations, but also farm-scale nutrient budgets, animal manure storage and treatment, manipulation of animal diets, redistribution of nutrients from areas of excess to where they are needed, and wider implementation of soil and water conservation practices. In Delaware and Maryland, they apply not only to farmers, but also to virtually all individuals, businesses, and organizations that could contribute to nonpoint nutrient pollution, except individual homeowners.

Source Reductions and Animal Manure Treatment: Fertilizer nutrient inputs can be reduced by the simple economic decision not to buy fertilizers when soil tests indicate no economic response to N or P is likely to occur. Reducing nutrient inputs via animal manures is more difficult, but some promising advances have occurred with P. Strategies now being implemented include using phytase enzymes to increase the digestibility of phytate P in the grain used for poultry and swine diets, thus decreasing the need to supplement the feed with inorganic sources of P (monogastric animals such as poultry and swine lack the enzyme needed to digest phytate P). In a similar approach, new corn varieties with lower phytic

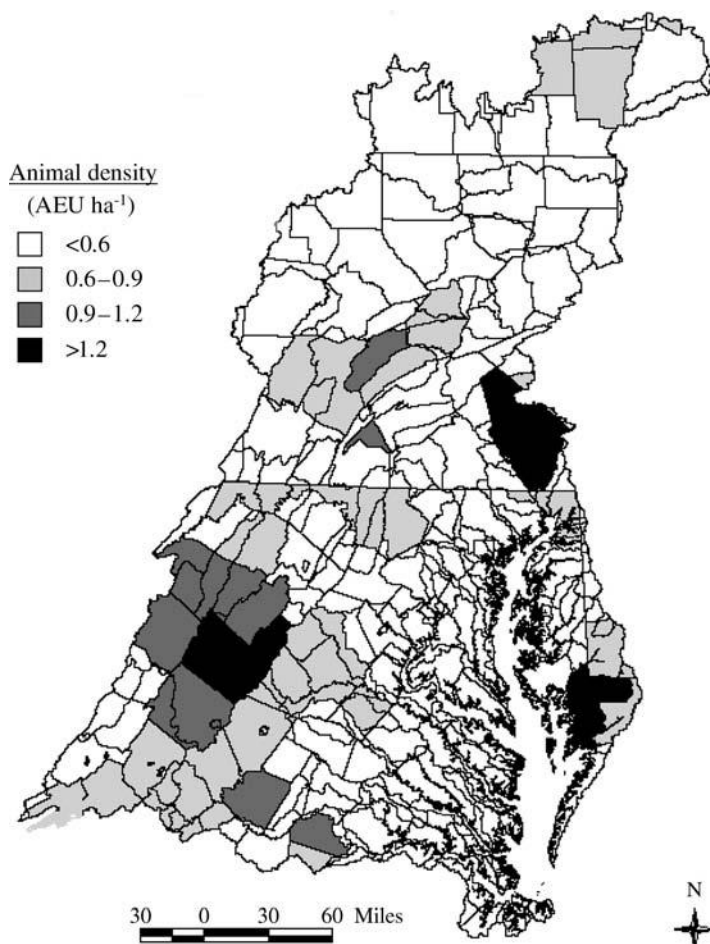


Figure 8.24 Illustration of the geographic concentration of animal production in certain regions of the Chesapeake Bay Watershed. (From Sims, J. T. and F. J. Coale, in *Agriculture, Hydrology, and Water Quality*, P. M. Haygarth and S. C. Jarris, Eds., CAB International, Oxon, U.K., 345–371, 2002. With permission.)

acid contents (“high available P” corn) are now available. These dietary manipulations have been shown to reduce the amount of P excreted by poultry and swine, and thus the overall P input to the watershed, by 20 to 50%. Wastewater treatment technologies are now being evaluated for use with animal manures, such as the addition of alum to poultry litters to decrease the solubility of P and emissions of NH_3 from farms.

Animal Manure Management: Farmers have always been encouraged to have their manure analyzed to determine the content of available nutrients. This is more widely done today because of an increased nutrient management educational effort and wider promotion of manure testing, such as by establishment of a state manure testing laboratory in Delaware. Once manure nutrient content is quantified, farmers are encouraged to apply manures using well-calibrated equipment at rates consistent with realistic yield goals and in a manner that maximizes crop nutrient uptake. Improved manure application equipment, such as “spinner spreaders” that can apply as low as 2 to 4 Mg/ha of manure are now widely available, as are extension fact sheets explaining how to calibrate spreaders. Proper timing of manure applications is encouraged, but not regulated at this time. For corn this is as close to spring planting as possible, while for small grains the best time is in the early spring. Manure applications are not recommended for soybeans because research showed that manure use did not increase yields and did increase $\text{NO}_3\text{-N}$ leaching below the root zone and the buildup of soil P to excessive levels. In many cases, as mandated by state laws, high soil P values now restrict manure applications to every third year and limit manure rates to crop P removal. This can require farmers to purchase and apply additional fertilizer N.

Fertilizer N Management: Corn is the major crop in the watershed that receives fertilizer N. Farmers that only use commercial fertilizer N normally apply a small amount of N at corn planting as a “starter” fertilizer and most of the fertilizer N in a single sidedress application about 6 weeks after planting. If irrigation is available, farmers also use “fertigation” to provide small amounts of fertilizer N in several midsummer applications. Farmers applying manures are encouraged to apply moderate rates close to planting and supplement manure N with sidedress fertilizer N or fertigation, if necessary. In all cases, the amount of sidedress N needed can be determined by the PSNT. The PSNT provides a quantitative assessment of soil N-supplying capacity and, if manure was applied, the amount of available N expected from the manure. Leaf chlorophyll meter (LCM) readings can also be used in spring and summer months to determine if additional N is required. A cornstalk nitrate test at the end of the season can indicate if excess N was present in soils during the growing season and thus be used to evaluate the overall success of the N management program.

Soil and Water Conservation Practices: Increased use of winter annual cover crops, riparian buffers, vegetated filter strips, and constructed wetlands to recover residual nitrate-N and dissolved P by plant uptake, enhance denitrification, and prevent particulate P loss are options now being widely promoted and subsidized by state and federal cost-share funds.

Bioenergy: The use of manures, particularly, poultry litters as a renewable energy source, to produce electricity and/or heat for local industries has attracted interest. Power plants in England, which now safely burn ~500,000 Mg of poultry litter/year, are one model for this option. Evaluation of air quality impacts and the development a market for the resulting ash are two key issues that must be resolved.

Redistribution and Alternate Uses: The potential to move surplus animal manure nutrients to other states or counties for use by farmers without animals is being supported through state-subsidized manure relocation programs in Delaware and Maryland. Use of poultry litter as a nutrient source for managed pine forests and for reclamation of minespoils is also under evaluation. Joint ventures to produce “pelletized” fertilizers from poultry litters, initiated by poultry companies and fertilizer manufacturers, are now well underway. Pelletizing these materials will produce a uniform product that is easier and more economic to transport and that can be enriched with commercial fertilizers to give specific nutrient ratios for differing cropping systems. A commercial pelletization plant that can process ~100,000 Mg of poultry litter per year opened on the Delmarva peninsula in 2002. Marketing efforts for pelletized litter emphasize movement of this material off the peninsula, to regions with nutrient deficits, and promote its value as an organic fertilizer.

Nutrient Trading: Nutrient trading means that, if expansion in one sector (e.g., municipal wastewater plant) in a watershed causes an increase in nutrient discharge, then nutrient reductions from another sector (e.g., agriculture) can be used to offset that increase. The guiding assumption is that it does not really matter where in a watershed the reductions in discharge occur, only that they do occur. Presumably, the sector desiring to sustain or increase its discharge would subsidize the efforts of the sector that provides the decrease and this trade would be economically beneficial to both. In the Chesapeake Bay watershed, wastewater treatment plants have adopted new technologies that reduce N and P discharge to surface waters. CAFOs that must continue to unnecessarily apply manure nutrients to cropland in the watershed, because they cannot relocate manures to other farms or identify alternative uses for manures, may be a market for these nutrient credits. Many questions remain about nutrient trading. Some are technical, such as the appropriate trading rate between a point source and a nonpoint source. That is, how many kilograms of land-applied manure N or P are equivalent to 1 kg discharged directly to water by a point source? Others are sociopolitical, such as the sustainability of allowing industries with sufficient financial resources to indefinitely discharge nutrients to the environment.

PROBLEMS

- 8.1 You are asked to evaluate the current approach used to apply N to corn in a watershed dominated by intensive dairy operations. Most farmers in the watershed apply the manure in late winter or early spring, about 1 month to 6 weeks before planting and then use a small amount of “starter” fertilizer at planting. You set up an “on-farm” demonstration where five rates of dairy manure are

- applied (0, 22, 44, 66, and 88 Mg/ha). The total N content of the dairy manure, as applied, was 1.4%, approximately 25% of which is plant available. At the end of the season you determine total N uptake at these N rates to be 90, 240, 270, 290, 310 kg N/ha. Calculate the nitrogen recovery efficiencies (NRE) for each approach using Equation 8.2 based on total N applied and “PAN” applied and discuss (a) the possible fates of any “unrecovered” N and (b) any steps that could be taken to improve N use efficiency in this watershed.
- 8.2 Explain the general relationship between N fertilizer application method and the efficiency of crop N recovery.
 - 8.3 The application of organic by-products such as manures, composts, and biosolids to leguminous crops is an issue currently being debated in many watersheds. Describe the pros and cons of the use of organic by-products on legume crops, such as alfalfa and soybeans. Do not confine your answer only to N management but consider all benefits and costs that are involved.
 - 8.4 A 3-year study in Maryland (Angle et al., 1993) showed that NO_3 leaching losses from dairy manure and inorganic fertilizer were consistently lower in a no-tillage situation than when the soils were conventionally tilled (plowed and disked). Explain how each of the following could have contributed to lower nitrate leaching with no-tillage: (a) cover crop use in no-till but not conventional till; (b) tillage effects on N immobilization, denitrification, and ammonia volatilization; and (c) improved soil moisture relations (more plant-available water in soils) with no-tillage.
 - 8.5 To conduct the PSNT, a soil sample is collected to a depth of 30 cm, dried rapidly, extracted with water or a salt solution, and then analyzed for soil $\text{NO}_3\text{-N}$. You extracted 5 g of soil with 100 mL of 2 M KCl and determined the concentration of $\text{NO}_3\text{-N}$ in the extract was 1.4 mg $\text{NO}_3\text{-N/L}$. The critical level for the PSNT for corn is 25 mg/kg. Based on your analysis, would you recommend sidedressing the corn with fertilizer N?
 - 8.6 One approach that has been shown to successfully reduce ammonia losses from animal manures is to add an acidifying material, such as “alum” $[(\text{Al})_2(\text{SO}_4)_3]$, directly to the manure/litter. Explain why this approach would reduce ammonia volatilization losses. Prior to recommending this practice for widespread use, what other factors would need to be considered?
 - 8.7 Explain why there has been interest, from both crop production and water quality perspectives, in the development of chemical compounds that can inhibit nitrification (see Figure 8.12).
 - 8.8 An engineering company initiates a project to revegetate a disturbed soil at a strip mine site with conservation grasses. The soil is highly acidic, deficient in nutrients, has poor structural properties and a very low organic matter content. The company wishes to add a very high rate of organic matter to improve soil structure and increase soil water-holding capacity. It has access to an organic by-product from a papermill (C:N ratio = 60:1), poultry manure from a nearby farm (C:N ratio = 6:1), and yard waste (leaves, grass clippings) compost from a local municipality (C:N ratio = 20:1). Which material would you recommend the company use, and why? What other steps will it need to take to successfully establish and maintain a grass cover? If economics forced the company to use one of the other sources, what steps should it take to counteract any problems it might encounter?
 - 8.9 A new, nonagricultural approach to reuse biosolids beneficially is “deep row tree farming.” In this system, large trenches (~50 cm wide and 75 cm deep) are filled with biosolids, covered with soil, and planted with poplar trees for 6 years, then harvested for timber. One of the concerns that had to be addressed in this system was the potential for nitrate leaching from the trenches. Explain how the environment in the trenches themselves (low oxygen, high moisture) and the types of plants being grown (perennials) affect the likelihood of nitrate leaching to shallow groundwaters.
 - 8.10 Urea is sometimes used as a “de-icing” agent at airports. A small, rural airport using urea began to notice algal blooms and declining water quality in nearby ponds. A state agency constructed an “artificial” wetland between the airport and the ponds to improve water quality. Explain the processes by which this wetland removes N from airport runoff waters.
 - 8.11 Assume you are asked to construct a “nutrient budget” for a 1235-acre (500-ha) dairy farm (500 cows, 300 heifers). The major crops grown are corn silage and alfalfa. All dairy manure produced on the farm is applied to the cropland where most (>75%) of the soils are now rated as either “optimum” or “excessive” in soil test P. Based on soil test results and crop yields, the total farmwide crop P requirement is determined to be 19,000 lb P_2O_5 /farm (3770 kg P/farm). You determine from farm records that each year the farm produces 5.2 million gallons (19.7 million L) of liquid manure with a total P content of 14 lb P_2O_5 /gallon (0.7 kg P/1000 L) and 3000 tons (2720 Mg) of solid manure,

with a total P concentration of 0.2% (2 g/kg). Calculate the total P surplus on the farm in lb P₂O₅/acre and in kg P/ha.

- 8.12 One of the most widely used practices for P management is soil testing. However, the many different soil P tests and units used to express the results are often confusing to farmers and others that are involved in interpreting the test results. You receive the results of a soil test and find that the soil test P value, using the Mehlich 1 soil test (0.05 N HCl + 0.025 N H₂SO₄), is 94 ppm P.
a. Convert these results to (a) mg P/kg; (b) lbs P₂O₅/acre; (c) kg P/ha.
b. You are told that laboratory comparison studies have developed the following “conversion” equation between the Mehlich 1 and Mehlich 3 soil tests:

$$\text{Mehlich 3-P (mg P/kg)} = [1.5 \times \text{Mehlich 1-P (mg P/kg)}] + 35$$

An upper limit for soil test P (Mehlich 3 test) of 300 lb P₂O₅/acre has been established in some states to identify soils where P should not be applied because of water quality concerns. Is the sample you received above or below this limit?

- 8.13 In some European countries, the degree of soil P saturation (DPS) is used to determine whether fertilizer or manure P can be applied to soils. For example, in the Netherlands, if a soil is >25% saturated with P to the depth of the mean high water table, P inputs are sharply limited or prohibited. Assume you extracted 1 g of topsoil with 40 mL of acid ammonium oxalate solution to determine DPS by the following equation:

$$\text{DPS (\%)} = 100 \times [(\text{Oxalate P, mmol/kg}) \div \alpha(\text{Oxalate Fe} + \text{Al, mmol/kg})]$$

The concentrations of Al, Fe, and P in the oxalate extract are 10.8, 7.4, and 4.5 mg/L, respectively. What is the DPS value in the topsoil (assume $\alpha = 0.5$)?

- 8.14 Explain why “starter” fertilizers are of value in crop production, even on soils that are considered to have “optimum” soil P levels.
- 8.15 The owner of a commercial turf farm near the Chesapeake Bay contacts you with the following analysis from a municipal biosolids compost: [N–P₂O₅–K₂O = 2.8–3.2–4.0]. A local waste management firm has told the owner that this compost can provide all the N, P, and K required to fertilize much of the soil on the turf farm. However, the grower is concerned, because of the proximity of the farm to the Chesapeake Bay, that using the compost may result in overapplication of P to this soil, which is already rated as “excessive” in P. Analyses of the soil at the site indicate that application of an 8–8–8 fertilizer (N–P₂O₅–K₂O) at 350 lb/acre is required. What rate of biosolids compost, in tons/acre, would be needed to equal the plant-available N added in 8–8–8 fertilizer (assume 20% of the total N in the compost is plant available)? How much P would be added in the biosolids compost at this rate and what effect would this have on the soil test P levels on the farm?
- 8.16 Constructing artificial wetlands has been suggested as a means to “trap” soluble and sediment-bound P moving from agricultural soils to surface waters. What are the advantages and disadvantages of this BMP for water quality protection?
- 8.17 Explain the physical and chemical principles by which buffer strips and grassed waterways operate to prevent nonpoint-source pollution of surface waters by soil P.

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PART III

Inorganic and Organic Contaminants

CHAPTER 9

Trace Elements

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9.1 INTRODUCTION

Trace elements are elements that are normally present at relatively low concentrations in soils, plants, or natural waters, and that may or may not be essential for the growth and development of plants, animals, or humans. With such a broad definition, trace elements obviously include a large number of elements with widely ranging chemical characteristics and effects on various organisms. Figure 9.1 is the periodic table of elements with shaded elements representing those that are not considered trace elements. Shaded elements (1) are present in relatively high concentrations in plants, soils, and natural waters and therefore do not fit the definition of trace elements; (2) have existed only as radioactive isotopes that have since decayed to daughter products; (3) do not occur naturally in the environment; or (4) are present only as inert gases. There is some debate whether certain elements should be classified as trace elements when present in high concentrations in soils or the Earth's crust, but in low concentrations in plants. Titanium (Ti), iron (Fe), and aluminum (Al) are three examples. They are not discussed in detail in this chapter, but they would be considered trace elements by our definition. Most discussions of trace elements do not include the radionuclides, many of which would also be trace elements by our definition and, thus, are discussed in this chapter.

9.2 TRACE ELEMENT CATEGORIES AND IMPORTANCE

A variety of terms are often used to describe trace elements or subsets of the elements that we have defined as trace elements. Micronutrients and heavy metals are two such terms. The use of *micronutrients* is avoided here because the term implies that the elements in question are essential for the growth and development of some organism, and many trace elements are not. Zinc (Zn) is essential for many organisms and would be a micronutrient while lead (Pb) is not essential and would not be a micronutrient. Both are trace elements. *Heavy metals* is another term that is avoided here because it generally refers to only metallic elements with an atomic weight greater than that of Fe (55.8 g/mol) or a density greater than 5.0 g/cm³, which also excludes many trace elements.

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Figure 9.1 Periodic table of the elements. Shaded elements are not considered trace elements because they exist in high concentrations in plants, soils, and waters; have existed only as radioactive isotopes that have since decayed to daughter products; do not occur naturally; or are inert gases.

For example, chromium (Cr) is a metal with an atomic weight less than Fe, and arsenic (As) and selenium (Se) are metalloids rather than trace metals. All these elements are important trace elements that are not heavy metals, although they are often mistakenly referred to as heavy metals. Other terms that have been used to describe trace elements include trace metals, microelements, minor elements, and trace inorganics.

Some 78 elements are considered trace elements based on Figure 7.1. It would not be possible, or even necessary, to discuss all of these in detail in this book. A simple means of reducing the number of elements considered would be to limit the discussion to those elements that are of concern because they are either essential or potentially toxic to plants, animals, or humans. By this method we might consider As, boron (B), beryllium (Be), cadmium (Cd), cobalt (Co), Cr, copper (Cu), fluorine (F), Fe, mercury (Hg), iodine (I), manganese (Mn), molybdenum (Mo), nickel (Ni), Pb, Se, tin (Sn), vanadium (V), and Zn. A description of the behavior of all these elements in soils is not possible here, although some are used as examples to illustrate general principles.

Another convenient way to categorize soil trace elements is by their expected chemical form in soils and soil solutions. *Cationic metals* are metallic elements that occur predominantly in the soil solution as cations. Examples are silver (Ag^+), Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} . *Oxyanions* are elements that are combined with oxygen in molecules with an overall negative charge. Examples are arsenate (AsO_4^{3-}), borohydrate ($\text{B}(\text{OH})_4^-$), chromate (CrO_4^{2-}), molybdate (MoO_4^{2-}), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). The *halides* are members of group VIIA in the periodic table and are present as anions in the soil solution. The halides are fluoride (F^-), chloride (Cl^-), bromide (Br^-), and iodide (I^-). The categories are not mutually exclusive, however, as some elements can occur in more than one category.

As will be shown, the chemistry of the soil determines the chemical species that dictates the behavior of the element, including factors such as leachability, bioavailability, risk to human health, and remediation strategies. In previous chapters we have discussed three important nutrient oxyanions, namely, nitrates (NO_3^-), orthophosphates (e.g., H_2PO_4^-), and sulfates (SO_4^{2-}). It is reasonable to expect the trace element oxyanions and the oxyanions of the nutrients to exhibit similar characteristics for properties such as sorption to soil solids, changes in oxidation state, formation of gaseous compounds, and microbial interactions. Similarly, we would expect the cationic metals to interact with the cation exchange sites of the soil the same as any other cation, although they are at a competitive disadvantage because of the relatively high concentrations of the major exchangeable cations calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). Trace elements that are cationic metals, however, do have more of a tendency to form both inorganic and organic complexes than the major exchangeable cations.

9.3 SOURCES OF TRACE ELEMENTS FOR THE TERRESTRIAL ENVIRONMENT

Soil trace elements have both natural and anthropogenic sources. Soil parent materials will contain trace elements; therefore, all soils are expected to have small quantities of the elements we have defined as trace elements. The issue of what constitutes typical trace element concentrations in soils arises occasionally. Usually this is in reference to a potential contamination problem and we want to know if the results from a soil analysis reflect a contaminated situation. Unfortunately, there is no straightforward answer to this issue as the natural variability in soil trace element concentrations can be quite high. Table 9.1 presents some normal soil concentrations for selected trace elements and some geochemically anomalous concentrations. A soil with a total Pb concentration of 600 mg/kg, for example, could represent a situation in which a soil with an original Pb concentration within the normal range was contaminated or a geochemically anomalous situation. Additional information is required to make the correct determination.

9.3.1 Mining and Smelting

Uses for trace elements are quite numerous, and, consequently, there are a variety of ways trace elements can enter the terrestrial environment and become an environmental concern. Historically, the mining and smelting of trace elements has created soil contamination problems of the greatest magnitude. Figure 9.2 is a scene in southwest Missouri showing some of the environmental problems associated with Pb and Zn mining. The material in the background is chat, a waste rock that can have Zn and Pb concentrations as high as 20,000 mg/kg (2% by weight). Fine particles selectively eroded from the chat piles have the potential of contaminating nearby soils and becoming sediments in surface waters, which greatly enlarges the area affected by the original mining activity. In addition, these chat piles are a source of dust that can result in Pb exposure to people across a wide area. Mining activities such as this produce primary contaminants consisting of waste rock, tailings, and slag. Secondary contamination occurs in groundwater beneath open pits and ponds, sediments in river channels and reservoirs, floodplain

Table 9.1 Selected Trace Element Concentrations in Soils at Normal and Geochemically Anomalous Levels

Element	“Normal” Range (mg/kg)	Metal-Rich Range (mg/kg)
As	<5 to 40	Up to 2500
Cd	<1 to 2	Up to 30
Cu	2 to 60	Up to 2000
Mo	<1 to 5	10 to 100
Ni	2 to 100	Up to 8000
Pb	10 to 150	10,000 or more
Se	<1 to 2	Up to 500
Zn	25 to 200	10,000 or more

Source: Bowie, S. H. U. and Thornton, I., Eds., *Environmental Geochemistry and Health*, Kluwer Academic, Hingham, MA, 1985.



Figure 9.2 Abandoned Pb and Zn mining site in southwest Missouri. (Photograph credit: Gary M. Pierzynski.)

soils affected by contaminated sediment, and soils affected by smelter emissions. River sediments reworked from floodplains and groundwater from contaminated reservoir sediments are tertiary contaminants. Substantial areas have been affected by such activities in Arizona, Colorado, Kansas, Missouri, Montana, Oklahoma, Pennsylvania, Utah, and Wyoming in the United States. Many other such areas exist around the world. Mining and smelting activities have caused widespread ecological damage because relatively large areas have been affected and the trace element concentrations in soils can be quite high.

9.3.2 Motor Vehicles

The use of motor vehicles has been a source of trace elements for the terrestrial environment. Motor vehicles emit Cd from diesel fuel; Zn and Cd from tire attrition; Ni, Cr, V, tungsten (W), and Mo from attrition of steel; and Pb from gasoline. The use of Pb in gasoline was phased out in the United States beginning in the 1970s, but it is still used in gasoline marketed in much of the world. The concentrations of certain trace elements in soils along roads that have been in use for a long time will undoubtedly be elevated. This problem is most severe in older urban areas. The use of motor vehicles has also led to trace element-contaminated soils indirectly through practices such as automobile battery recycling and the use of automobile salvage yards.

9.3.3 Urban Issues

Paints are a major source of Pb in the environment. Similar to Pb in gasoline, Pb in paint was banned more than 25 years ago (1978) in the United States. However, homes and other structures built prior to the ban still have painted surfaces. As the paint on the exterior surfaces of buildings weathers, the Pb ends up in the soil. Similarly, paint from interior surfaces can become a component of house dust (as does the soil from outside the building), and produce a significant exposure pathway for people living in that environment. Paint chips can also be ingested directly by children. Obviously, older homes that are not well maintained pose the greatest risk.

It is logical to conclude that urban soils will generally have higher soil trace element concentrations than rural areas (except mining areas) due to their proximity to more trace element sources. Figure 9.3 shows a general decline in Cu, Ni, and Pb concentrations in forest floor and soil samples with distance from the center of New York City, illustrating the decline in trace element concentrations with distance from a generalized source. Still, in rural areas, we can find evidence of the use of trace elements by society. Figure 9.4 shows an increasing trend of Pb in the wood of American beech trees in Virginia with time. The sharp increase in Pb concentrations in the late 1800s corresponds to the industrialization of society. Lead concentrations then decrease until 1950 when they begin to increase again corresponding to the introduction of leaded gasoline. The subsequent decrease corresponds to the ban on leaded gasoline that was implemented about that time.

9.3.4 Rural Issues

Land application of by-products, either as a beneficial reuse or as a disposal strategy, can lead to trace element contamination of soils. Biosolids, the solid material remaining after municipal wastewater is treated, may enrich soils with trace elements particularly if the municipal wastewater treatment plants receive industrial as well as domestic inputs. This subject has been the source of considerable debate within the scientific community in recent years. In 1992, the U.S. Environmental Protection Agency (EPA) released the National Sewage Sludge Rule developed under the national Clean Water Act (40 CFR, Part 503). Commonly known as the Part 503 Rule, it establishes a series of limits for trace elements in biosolids that must be followed when biosolids are applied to land. To ensure that the agronomic biosolids rate does

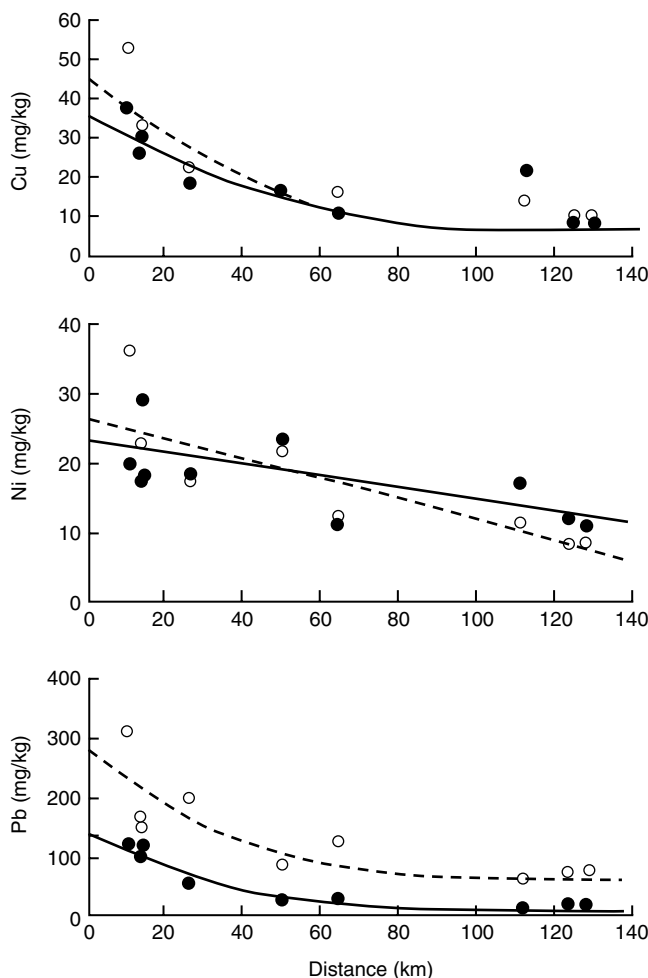


Figure 9.3 Forest floor and soil trace element concentrations as a function of distance from Central Park, Manhattan, New York City. Open circles represent forest floor and closed circles represent soil values. (From Pouyat, R. V. and McDonnell, M. J., *Water Air Soil Pollut.*, 57/58, 797, 1991. With permission.)

not apply excessive quantities of trace elements or other pollutants, monitoring of biosolids composition is required by permit. Four types of “pollutant limits” are in the Part 503 Rule (Table 9.2). *Ceiling concentration limits* are established to ensure that excessively contaminated biosolids are not applied to soils (e.g., 85 mg/kg for Cd). *Pollutant concentration limits* are used to determine if a biosolid is of “exceptional quality (EQ)” (e.g., <39 mg/kg for Cd). Use of EQ biosolids still requires a permit but the requirements to track long-term loading rates or maintain records and monitoring are not as stringent. *Cumulative pollutant loading rates* (CPLRs: total quantities of each pollutant that can be applied to a site) were also established in the Part 503 Rule to define the total length of time a site can receive biosolids. For example, if a municipality applies biosolids at appropriate rates for grain crops, and this adds 1.0 kg/ha/year of Cd, then the site can be used for 39 years. At issue is the degree to which enrichment should be allowed, and this is examined further in our discussion of risk assessment in Chapter 13. Similarly, animal manures may contain elevated levels of trace elements such as As and Cu that are present in livestock rations for various reasons.

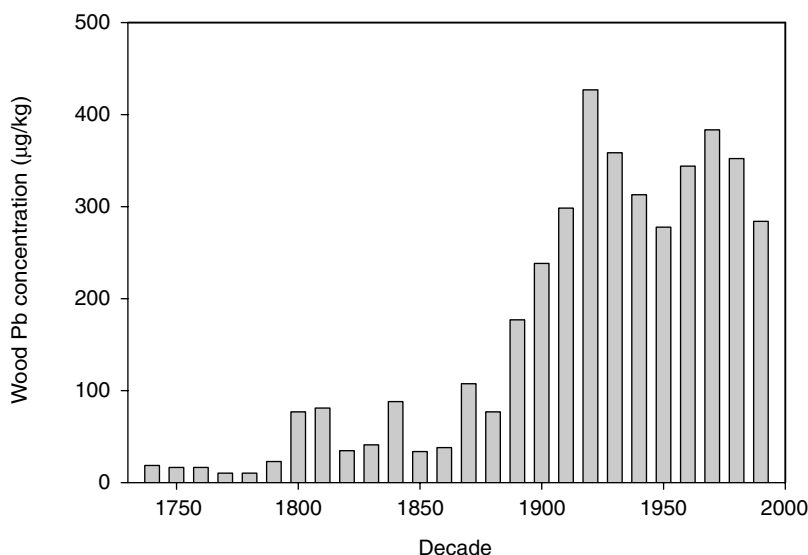


Figure 9.4 Concentrations of Pb in wood from American beech trees in Virginia over time. (Data from Fisher et al., 2003.)

Products sold as inorganic fertilizers may be enriched in certain trace elements. Cadmium and other nonessential elements may exist in the materials that were used to make the fertilizers and end up in the finished product. Rock phosphate is the primary source of phosphorus (P) for fertilizer and can be a carrier for unwanted trace elements. These impurities are an integral part of the ore. In some unusual cases industrial by-products containing Zn, as well as some other nonessential trace elements, were processed into a Zn-containing fertilizer (Zn as a micronutrient in this case). This generated considerable public outcry since the initial by-products were classified as hazardous waste and the materials were then legally applied to land as fertilizers. While there are no widespread reports of damages from these practices, the public is demanding closer scrutiny of all fertilizer materials. Table 9.3 provides averages and ranges for As, Cd, and Pb concentrations in commercial inorganic fertilizers and for biosolids and poultry litter for comparison. In general, the phosphate fertilizers have higher Cd concentrations than the other materials. Trace element concentrations in blended and micronutrient fertilizers are highly variable.

9.3.5 Other Sources

A variety of other trace element uses and sources for contamination of the terrestrial environment are less significant. The mining and use of materials such as coal or iron ore often lead to trace element-contaminated soils as well. In Wyoming and Idaho, surface mining for coal or P exposes Se-containing overburden that would not otherwise interact with the environment. Metal recycling facilities, particularly for metals like Cu and brass, have been known to emit significant amounts of trace elements. Disposal of batteries containing Pb, Ni, Cd, and other trace elements is another example.

Widespread trace element contamination of soils has occurred in some areas of the world. Our knowledge of the behavior of these elements indicates that soils are difficult to decontaminate once the contamination has occurred. Thus, society is increasing efforts to prevent trace element contamination. Simultaneously, efforts are under way in some areas to mitigate the negative effects of existing contamination as our knowledge of the human health and ecological risks increases. Soil remediation is discussed at length in Chapter 12.

Table 9.2 Pollutant Limits for Land Application for Municipal Biosolids — Criteria for Land Application Programs as Defined in the 1992 National Sewage Sludge 503 Rule of the EPA

Trace element	Concentration Limit (mg/kg)		Loading Rate Limits	
	Ceiling	Pollutant	Cumulative (kg/site)	Annual (kg/ha/year)
As	75	41	41	2.0
Cd	85	39	39	1.9
Cu	4300	1500	1500	75
Pb	840	300	300	15
Hg	57	17	17	0.85
Ni	420	420	420	21
Se	100	100	100	5.0
Zn	7500	2800	2800	140

Definitions of pollutant limits are as follows:

Ceiling concentration limit: Maximum allowable concentration of a pollutant in biosolids that are to be land applied. Ceiling concentration limits are either the 99th percentile concentration of a pollutant as identified in the National Sewage Sludge Survey or the pollutant limits identified in the biosolids risk assessment process.

Pollutant concentration limit: Most stringent, risk-based pollutant limit in the 503 Rule. Pollutant concentration limits define the “no-adverse-effect” concentration where biosolids can be safely land applied without the need for record-keeping of cumulative pollutant loading rates. Biosolids that meet these concentration limits are sometimes referred to as “exceptional quality” biosolids and can be land applied as freely as other fertilizers and soil conditioners.

Cumulative pollutant loading rate (CPLR): CPLRs apply to biosolids with concentrations above the pollutant concentration limit. Permitting requirements mandate that accurate records be kept of the amount of pollutants applied to a site from biosolids subject to CPLRs. Once the CPLR is attained, biosolids can no longer be applied at the site. Even at the CPLR, risk assessment showed that the pollutant loading rate is protective of public health and the environment.

Annual pollutant loading rate (APLR): APLRs apply only to biosolids that are sold or given away in a bag or container and identify the maximum amount of a pollutant that can be applied to a site in 1 year. APLRs were derived by dividing CPLRs by 20, assuming that a 20-year site life where biosolids are land applied is reasonable. APLRs are used with bagged and containerized biosolids because of the difficulty in maintaining long-term records when biosolids are applied to situations such as lawns, home gardens, public contact sites (e.g., parkland).

Source: U.S. EPA, 1993.

9.4 ADVERSE EFFECTS

It is difficult to summarize all adverse effects due to trace elements because of the large number of elements and the fact that each element can cause a number of different problems. Human health effects are generally of greatest concern. As shown below, an astonishing number of people are affected by trace element toxicities. Impacts on our ability to produce food are also of great concern. Here the impacts of the trace elements on food quality as well as plant and animal productivity are important. Of growing interest in recent years are the ecological impacts of trace elements in the terrestrial and aquatic environments. All the effects can be placed into four broad categories, which are discussed individually: (1) human health, (2) animal health, (3) effects on plants, and (4) effects on aquatic ecosystems. Ecological impacts are divided among the final three categories.

Any trace element can have an adverse effect on any organism if the dose is high enough. Some of the trace elements are essential for plants, animals, or humans, which further complicates issues. Generally, exposure of organisms to high doses of trace elements is uncommon and, therefore, not considered an environmental problem. Table 9.4 indicates the species that are most commonly at

Table 9.3 Average As, Cd, and Pb Concentrations (mg/kg) in Selected Inorganic Commercial Fertilizers and Soil Amendments

Material	Fertilizer Grade	As	Cd	Pb
Soil Amendments and Liming Materials^a				
Limestone	—	2.2	6.2	33.9
Gypsum	—	1.3	0.9	4.4
Phosphate Fertilizers^a				
Triple superphosphate	0-20-0 ^b	4.8	110	2.0
Monoammonium phosphate	11-23-0	8.1	74.1	2.6
Diammonium phosphate	18-20-0	4.9	38.1	4.0
Soft phosphate rock ^c	Unknown	13.0	130	13.0
Other Fertilizers^a				
Muriate of potash	0-0-50	0.4	0.8	3.3
Urea ^c	46-0-0	0	0	0
Blended ^c	11-5-0	11.2	95.0	3600
Zinc sulfate	—	2.6	32.3	203
By-Products				
Poultry litter ^d	—	37.6	0.7	1.7
Biosolids ^e	—	4.6	3.3	82.1

^a California Department of Food and Agriculture, 1998.^b % N, P, and K by weight.^c One sample only.^d Smith et al., 2000.^e Stehouwer et al., 2000.**Table 9.4 A Summary of Species Most Commonly Affected by Toxicities of Selected Trace Elements**

Element	Species Adversely Affected				
	Humans	Animals	Aquatic Organisms	Birds	Plants
Cd	X	X	X	X	X
As, Pb, Hg, Cr, Se	X	X	X	X	
Cu, Ni, Zn			X		X
Mo, F, Co		X			
B					X

Source: A. L. Page, personal communication, 1992.

risk due to exposure to elevated doses of 13 important trace elements. Note, for example, that Pb is of concern for humans, animals, aquatic organisms, and birds, but rarely induces phytotoxicities as compared with B for which phytotoxicities are of primary concern.

9.4.1 Human Health

The primary routes of exposure of humans to trace elements in soil are through food chain transfer and by direct ingestion of soil particles (see Figure 1.2). Documented cases of acute trace element poisonings in humans due to elevated soil trace element concentrations are rare. Documented cases of chronic adverse health effects due to trace element exposure through food chain transfer or direct ingestion of soil are more numerous. The number of people affected by trace element poisoning worldwide is quite astounding, as shown in Table 9.5. Note that soil is the primary recipient of global emissions of trace elements.

Cadmium and Pb can be used to illustrate the two general exposure routes for humans. Each can have profound health effects on humans, but means of exposure are quite different due to their chemical behavior in the soil environment and the concentration ranges at which they occur in contaminated soils. Cadmium is readily taken up by plants (a high bioavailability for plant uptake) and food chain transfer is the primary route of exposure. An often-cited example deals with Japanese farmers suffering from Cd toxicity after long-term exposure to Cd-enriched rice. Two symptoms of Cd toxicity are renal dysfunction and *itai-itai* disease. *Itai* is Japanese for “ouch,” and the disease is characterized by Cd-induced bone loss that produces localized, severe pain in the joints of victims. The Cd-enriched rice had been grown in paddies polluted by Pb and Zn mining and smelting operations. There is a geochemical association between Zn and Cd, and therefore Zn-contaminated soils are often Cd contaminated as well. Table 9.6 indicates that rice grown in areas having >10% morbidity had Cd concentrations as much as 14 times higher than rice grown in nonpolluted areas. This situation was exasperated by the general poor nutrition of the population, which made people more susceptible to Cd toxicity. Food chain transfer of Cd is often the limiting exposure pathway (negative effects at the lowest soil Cd concentration) for risk assessments conducted for trace element-contaminated soils.

For trace element-contaminated soils, Pb concentrations are generally much higher than Cd concentrations (see Table 9.1). Despite the higher soil Pb concentrations, plant uptake of Pb is very limited (i.e., low bioavailability for plant uptake). In order for substantial exposure to occur, the soil itself must be ingested, and because soil Pb concentrations can be fairly high this can result in a physiologically significant dose of Pb to the recipient. It is also recognized that the bioavailability of soil Pb for the human receptor can vary considerably. That is, two soils with equal total Pb concentrations ingested in equivalent amounts can produce differing effects (see Figure 1.3). Lead has a number of physiological effects on the human body and infants and children are at much greater risk than adults. One such effect is impairment of mental development that causes children with chronic

Table 9.5 Estimated Magnitude of the Extent of Trace Element Poisonings

Element	Global Emissions (1000 Mg/year)			People Affected	Comments
	Air	Water	Soil		
Pb	332	138	796	>1 billion	Blood Pb > 20 µg/dL
Cd	7.6	9.4	22	500,000	Producing renal dysfunction
Hg	3.6	4.6	8.3	80,000	Certified Hg poisonings
As	18.8	41	82	>100,000	Skin disorder and H ₂ O As >2 µg/L

Source: Nriagu, J. O., *Environ. Pollut.*, 50, 139, 1988.

Table 9.6 Cadmium Concentrations (mg/kg) in Rice by Prevalence of *Itai-Itai* Disease

Rice Type	Area	
	High Endemic ^a	Nonendemic
Nonglutinous		
Polished	0.52	0.048
Unpolished	0.54	0.079
Glutinous		
Polished	1.03	0.071
Unpolished	1.12	0.150

^a >10% morbidity.

Source: Tsuchiya, K., in *Cadmium Studies in Japan: A Review*, K. Tsuchiya, Ed., Elsevier, New York, 1979.

exposure to Pb to score lower on IQ tests than children not exposed. Blood Pb concentrations are often used as a screening test for Pb exposure in children and the levels have been steadily falling in the United States because Pb has been eliminated from gasoline and paint. People living in older urban areas will typically have elevated Pb exposures due primarily to the use of leaded house paints. The current guideline for children is to have the blood Pb concentration <10 µg/dL, a value that has been steadily decreasing from a high of 60 µg/dL prior to 1970. In areas with Pb-contaminated soils as many as 25% of the children will exceed the 10 µg/dL guideline. For the period of 1976–1980 (as leaded gasoline was being phased out) the average blood Pb concentration for children in the United States was 14.9 µg/dL with 88% >10 µg/dL, while in 1999–2000 the average was 2.2 µg/dL with 2.2% >10 µg/dL. The number of children adversely affected decreased from 13.5 million to 434,000 in that same time period. More recent studies suggest significant health effects when blood Pb levels are <10 µg/dL, so further evaluation of the guideline may be in order.

Two other trace elements that are somewhat notorious for human health effects are Hg and As. The phrase “mad as a hatter” is derived from individuals who used mercuric nitrate (Hg(NO₃)₂) in the making of felt hats and treatment of furs. The symptoms of this subacute Hg poisoning included tremors, vertigo, irritability, moodiness, and depression. Liquid (elemental) Hg evaporates at room temperature and inhalation of Hg vapor can lead to significant exposure from this form of Hg. This was once significant in certain occupations such as mining where Hg amalgams were used to concentrate metals such as Au. This is also the reason attempts are made to vacuum up Hg droplets after an Hg spill. The most extensive exposure route for humans today is through methylmercury (Hg(CH₃)₂) in seafood. A highly publicized case of this occurred in Japan following the dumping of Hg into Minamata Bay and the subsequent consumption of fish from the bay by local residents. This acute form of Hg poisoning, since called Minamata disease, manifested itself in mental retardation, cerebral palsy, and fetus mortality in the children of the exposed population. While outbreaks as serious as that in Japan have not occurred since, health advisories against consumption of seafood because of Hg are still common today. The methylated forms of Hg are formed readily in the anaerobic environment found in sediments.

Human health effects from As vary depending on the dose received and the chemical form of As. General symptoms include weakness, muscular aches, hearing loss in children, and possibly skin cancer. Exposure most often occurs from drinking water, although soils that have received arsenical pesticides, such as orchards and areas where vegetables were produced, can be highly contaminated. In these situations, the direct consumption of soil is the primary route of exposure, similar to Pb. A serious problem exists in western India and Bangladesh today where an estimated 200,000 people have As-induced skin lesions. This is a result of consumption of As-contaminated drinking water. New wells were drilled into high-As sediments to supply water for irrigation to improve agricultural productivity, and the water was also used for personal consumption.

Of increasing interest recently is the possibility of *subclinical effects* due to exposure to slightly elevated amounts of trace elements. Subclinical effects represent symptoms or diseases not easily diagnosed by medical examination. Attention deficit disorder, hyperactivity, or low IQ test scores are three relevant examples. Epidemiological studies are required to detect statistically significant trends. This is an area needing much study.

9.4.2 Animal Health

Animal health effects include domestic animals and wildlife. Toxicities of Mo in livestock (*molybdenosis*) and Se in livestock and wildlife (*selenosis*) are two relatively common trace element animal health problems. Ruminant animals are the most susceptible to molybdenosis, a Mo-induced Cu deficiency. Some soils have naturally occurring high Mo concentrations and can produce forages that can induce molybdenosis in grazing animals. Soils can be naturally enriched in Mo or become enriched due to poor-quality irrigation water or Mo-rich biosolids additions. Selenium problems are much more widespread. Outcroppings of seleniferous sedimentary rocks occur in certain regions throughout the United States and elsewhere. In semiarid to arid regions, the associated soils may produce plants with Se concentrations that are harmful to animals if consumed regularly. Coal mining activities may also bring seleniferous materials to the surface. The Kesterson Wildlife Refuge area of central California represents a situation where agricultural activities have led to some serious outbreaks of Se poisoning in wildfowl. Irrigated cropland produced drainage water with a high Se concentration. As this water flowed into the Kesterson area, it was further concentrated by evaporation and produced widespread Se toxicity problems for aquatic life and waterfowl.

9.4.3 Phytotoxicities

Phytotoxicity refers to reduced yields or death of plants by substances in the soil. Symptoms for trace element-induced phytotoxicities can include stunting, chlorosis, necrosis, and death of the plant. Trace elements most often associated with phytotoxicities are B, Cu, Ni, and Zn. Phytotoxicity problems are of concern for two primary reasons. First, the reduction in soil quality induced by elevated trace element concentrations can reduce both the quantity and the quality of the food produced from that soil. An example is illustrated in Figure 9.5. Here the relative yield of three crops declines as the $\text{Mg}(\text{NO}_3)_2$ -extractable soil Cu concentration increases. When the extractable Cu concentration exceeds that shown by the vertical dashed line, relative yield is predicted to decline by >10%. In this situation, Cu was being studied because of potential phytotoxicities from Cu additions due to swine manure applications. Manure-amended soils had not, in general, reached the critical level of 2 mg/kg of $\text{Mg}(\text{NO}_3)_2$ -extractable soil Cu. The second reason relates to areas where vegetation is sparse because of trace element phytotoxicities so that wind and water erosion can occur uninhibited. These conditions often exist around sites where metal mining or smelting once took place (Figure 9.2). In the case of Figure 9.2, elevated soil Zn caused phytotoxicity problems, but was not a direct human health threat. The lack of vegetative cover allowed further dispersal of the Cd and Pb present at these sites, thereby increasing human exposure indirectly. Direct inhalation of windblown dusts from such areas can also be an exposure route for humans and animals.

9.4.4 Aquatic Environments

The effects of elevated concentrations of trace elements in aquatic environments are extremely difficult to assess, due in part to the mobility of some of the trace element species and the difficulty in separating out the effects of contaminated water from contaminated sediment. Soil erosion is the primary mechanism by which trace elements are transferred from the terrestrial to the aquatic environment. The enrichment ratios for most trace elements are ≥ 1 . Aquatic species

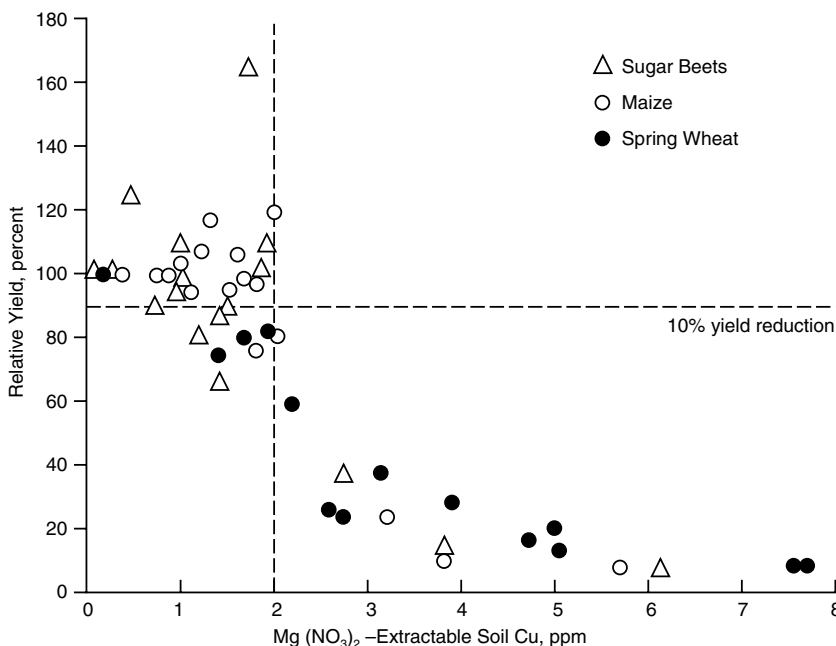


Figure 9.5 Relationship between $\text{Mg}(\text{NO}_3)_2$ -extractable Cu in soil and crop yield. (From Lexmond, T. M. and deHaan, F. A. M., in *Proc. Int. Seminar on Soil Environment and Fertility Management in Intensive Agriculture* (Tokyo), Soc. Sci. Soil Manure, Tokyo, 1977. With permission.)

can be divided into groups of plants (phytoplankton and benthic), invertebrates, and fish. The species can be characterized according to their diversity, productivity, and density. Diversity refers to the number of species present in a given area, productivity refers to the weight or size of individual organisms, and density refers to the number of a given species present in a given area. The effects of trace elements are generally to reduce the diversity, productivity, and density of aquatic organisms.

9.5 TRACE ELEMENT CYCLES IN SOILS

Detailed soil nitrogen (N), P, and sulfur (S) cycles have been presented in Chapters 5, 6, and 7, respectively. Since the trace element category includes a large number of elements, it would be impractical to present individual soil trace element cycles. Figure 9.6 presents a generalized soil trace element cycle that illustrates processes and transformations that are important for most trace elements. Trace element inputs to the soil cycle are discussed in Section 9.2. Most of these processes should be familiar to the reader based on previous discussions of the soil N, P, and S cycles. The influence of these processes on bioavailability are discussed in the next section and the use of our knowledge of these processes for soil remediation is discussed in Chapter 12.

9.5.1 Soil Solution

The soil solution is the focal point of any soil element cycle. The soil solution is where plant roots and other soil organisms interact with essential and nonessential elements in the soil. Plant uptake of trace elements occurs from the soil solution and its composition reflects the interactions between soluble species and the solid phases. For example, strongly adsorbed species or those of sparingly soluble compounds will be present in the soil solution at very low concentrations, and vice versa.

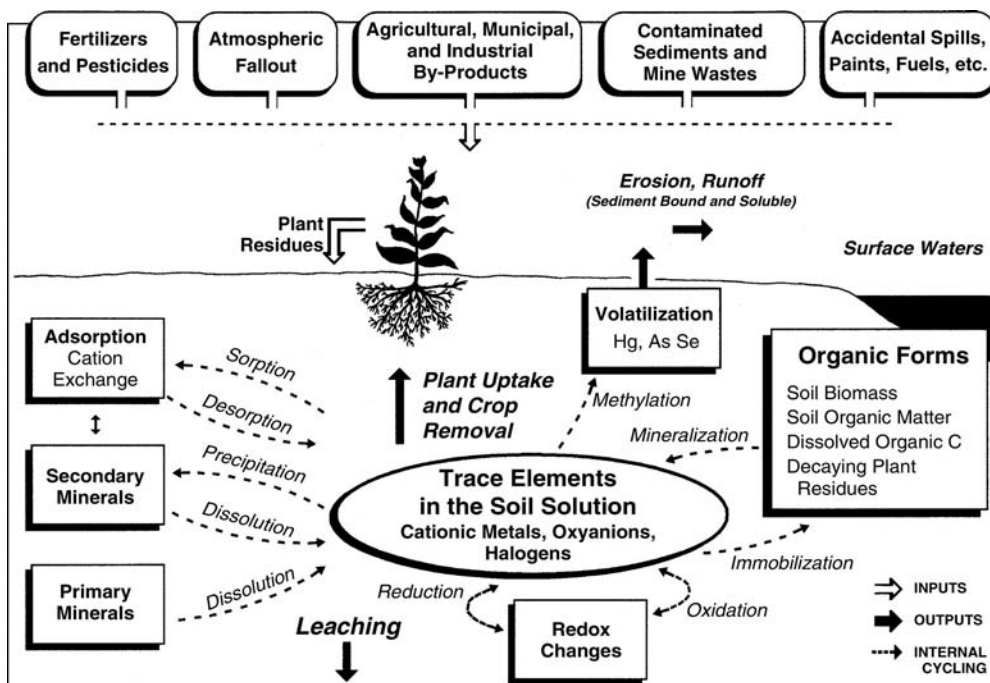


Figure 9.6 Generalized soil trace element cycle.

The primary trace element species of interest in the soil solution are the cationic metals, oxyanions, and halides, as described earlier. These species also form a variety of soluble complexes with other elements and with dissolved organic carbon (C) constituents. Sometimes these soluble complexes are a combination of two ions, such as CdCl^+ , or are a combination of a trace element and elements that are normally present in much higher concentrations in soils, such as CaSeO_4^0 . Techniques are available to speciate the total amount of a trace element in the soil solution into its constituents (e.g., $\text{Cu}_T = \text{Cu}^{2+} + \text{CuOH}^+ + \text{CuCO}_3^0 + \dots$). However, the chemistry and environmental significance of this speciation is beyond the scope of this book (see Supplementary Materials for several resources on this topic).

9.5.2 Sorption

Most trace elements undergo some sort of sorption processes with the solid phases in the soil. *Sorption* is a generic term that refers to the tendency of a substance to be retained by the soil solid phases (see Chapter 3). Substances that are strongly retained are relatively immobile in soils and may have a low bioavailability. There are three primary mechanisms responsible for the sorption phenomenon for trace elements: adsorption, cation exchange, and the formation of insoluble secondary minerals. *Adsorption* generally refers to the formation of a chemical bond between soluble substances and the soil solids. Molybdate (MoO_4^{2-}), for example, is adsorbed by Fe and Al oxides in a fashion similar to orthophosphate (PO_4^{3-}). Two important oxyanions, nitrate (NO_3^-) and orthophosphate, which have been discussed already in this book, have very different adsorption characteristics. Nitrate undergoes little if any adsorption, whereas orthophosphates are strongly adsorbed. The behavior of most of the trace element oxyanions is intermediate relative to nitrates and orthophosphates. The reason that selenosis in livestock is more prevalent in arid or semiarid

regions is because SeO_4^{2-} is not strongly adsorbed by the soil, is not leached from the soil, and is readily available for plant uptake. Molybdate is less prone to leaching than SeO_4^{2-} but is still more mobile than orthophosphates.

Cation exchange refers to the electrostatic attraction between cations in the soil solution and the negatively charged soil solids, both clay minerals and soil organic matter. The cationic trace elements must compete for exchange sites against the predominant cations in soils (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and generally do so effectively. There are differences between the cationic metals, as was illustrated earlier for Cd and Pb and their availability for plant uptake.

Secondary mineral formation is generally not important in uncontaminated soils because the trace element concentrations are low and undersaturated with respect to the solubilities of possible solid phases. In contaminated soils, however, trace elements may form secondary minerals. When secondary minerals do form, the possibility exists that the solid phase will control the concentration (more accurately, the activity) of that element in the soil solution, which can greatly influence the trace element bioavailability. Examples include wulfenite (PbMoO_4), hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$), and franklinite (ZnFe_2O_4).

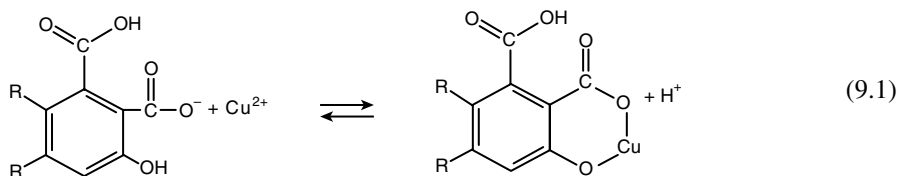
In most soils the dissolution of primary minerals is of minor importance because the quantities of such minerals are quite low. In areas where trace element-rich deposits are near the surface, the dissolution of primary minerals can be a significant source of trace element enrichment for soils. We have already described an example with Se. Other elements where this might be a concern include Cr, Cu, Ni, Pb, and Zn.

9.5.3 Redox Conditions

Redox changes are important for a number of trace elements including As, Cr, Hg, Mn, and Se. The chemistry behind the redox changes is beyond the scope of this text, but the reader should be aware that such changes can greatly influence the fate and transport of the trace element in the environment as well as the toxicological characteristics. Chromium, for example, exists as both Cr^{3+} and CrO_4^{2-} (with Cr(VI)). The hexavalent Cr is much more toxic and mobile in the environment compared with the trivalent form. The Kesterson Wildlife Refuge situation was a result of the oxidation of reduced forms of Se to SeO_4^{2-} , which is more mobile and which allowed Se to leach from irrigated soils and eventually reach the refuge. There are indirect effects of redox as well. Most of the cationic metals do not undergo changes in oxidation state under conditions found in soils but can form insoluble sulfides under reducing conditions (see Figure 7.4). This is one mechanism by which wetlands can accumulate trace elements.

9.5.4 Organic Species

Organic forms can be significant for certain trace elements. The amounts present in soil biomass are generally low and of little importance. Certain trace elements form strong complexes with functional groups in soil organic matter or dissolved organic C, which greatly influences the interactions with the soil solution. The reaction given below illustrates this process for Cu, which is generally strongly associated with the organic C fraction in soils. These chelation reactions are obviously important for the cationic metals. Oxyanions can also interact with soil organic matter by forming bonds with other cations that are already associated with the organic C fraction. Mercury forms a variety of methylated compounds under reducing conditions that are readily accumulated by aquatic species. The consumption of seafood is a major route of exposure for Hg to humans, as discussed earlier.



9.5.5 Losses

Volatilization is only important for a few trace elements, notably Hg, As, and Se. Elemental Hg can form a vapor and be lost from soils or sediments as a gas. Mercury, As, and Se can be methylated by soil microorganisms and some of these methylated forms are gases. Dimethylselenide, for example, can be formed from Se-contaminated soils and this process has been explored as a means of remediating Se-contaminated soils and sediments.

Runoff and erosion losses of trace elements can be a major transport mechanism in the environment. Soil erosion occurs when soil particles are detached and then transported across the landscape. Vegetation and plant residues greatly reduce soil erosion because they absorb the impact of raindrops, thereby reducing detachment of soil particles, and they decrease the flow of water across the soil surface, which inhibits the transport process. If phytotoxic conditions have prevented or limited plant growth, then the transport of trace elements in runoff becomes more prevalent (Figure 9.2). Aquatic ecosystems are sensitive to trace element contamination so significant negative effects can occur with only small inputs of trace elements.

9.5.6 Plant Accumulation

In situations where plant residues are not removed from the landscape, soil trace elements are continually recycled through plant uptake and decomposition of plant residues. Where biomass removal occurs (e.g., agricultural or turf grass scenarios), significant amounts of trace elements can be removed from the soil through plant uptake. In general, plants do not accumulate high concentrations of trace elements so removal rates from plant uptake are considerably less than those for plant nutrients such as N or P. Trace elements in plants represent an exposure route for any organism that consumes the plant tissue, so the concentration issue is not trivial. Certain types of plants are known to *hyperaccumulate* some trace elements. There are Se hyperaccumulators that are native to rangeland in arid and semiarid regions. When these are present, grazing animals can greatly increase their risk for selenosis when these plants are consumed rather than other species with much lower Se concentrations. Scientists have proposed using hyperaccumulators of As, Zn, Pb, and other trace elements as a means of removing trace elements from soils, as discussed in Chapter 12.

9.6 BIOAVAILABILITY OF TRACE ELEMENTS IN SOILS

As described in Chapter 1, bioavailability is related to the possibility that a substance can cause an effect, either positive or negative, on an organism. This concept is vitally important for trace elements for a variety of reasons, although we must take a broad view of the subject and carefully identify both the organism of interest and the effect. Once the organism and the effect are identified, the factors influencing bioavailability can be studied. Small changes in bioavailability can dramatically influence the effect. Two examples are used, one involving plants as the organism of interest and the other involving humans. Of course, any of a number of organisms could be used including soil invertebrates, domestic or wild animals, or even birds.

9.6.1 Plants

There is a long history of research dealing with the bioavailability of soil trace elements to plants. Early work focused on deficiencies of trace elements that were essential for plant growth, including B, Cu, Fe, Mn, Mo, and Zn. When these elements are not present in soil in sufficient available quantities for plants, dramatic increases in growth can be realized by increasing the bioavailability of the trace element. This work demonstrated that the total trace element concentration in a soil is a poor predictor of trace element bioavailability. In other words, a soil could have a high trace element concentration and plants would be deficient in that element while another soil could have a lower total concentration but not have problems with plant deficiencies. Further, when some trace elements were added to the soil, the deficiency problems were not solved. Many of these observations could be related to soil pH. For example, Fe, typically present in relatively high concentrations in soils, can have very limited availability for plant uptake when the soil pH is high. The direct application of Fe salts to high-pH soils is a notoriously poor way to correct Fe deficiencies because the soluble Fe that is added precipitates as insoluble secondary minerals with low plant availability. For contaminated soils, we many need to be concerned with phytotoxicities when trace element bioavailability becomes too high.

The bioavailable fraction of trace elements in soil is some subfraction of the total trace element fraction that best predicts the response. Here, this response generally refers to plant uptake of the trace element but could also include yield increases if the trace element is an essential micronutrient and the plant is deficient. Trace element bioavailability to plants is strongly related to the concentration and speciation of the element in the soil solution because this is where the plants get their trace elements. The *free ion activity model* (FIAM) suggests that plants take up one or two forms of trace elements from the soil solution. Generally, for cationic trace elements this soluble specie is the free ion form. Hence, one key to understanding bioavailability to plants is to understand the factors that influence the soil solution concentration of the soluble species that are taken up by the plant.

Copper can be used as an example to illustrate some of the processes involved in bioavailability to plants along with our soil trace element cycle. We could easily measure the total Cu concentration in the soil solution (not to be confused with the total Cu concentration in the soil) with atomic absorption spectrophotometry. As described earlier, the concentration would be denoted Cu_T and is a summation of various soluble Cu species. Based on the soil trace element cycle, we see that the free Cu^{2+} ion can undergo adsorption reactions, precipitate as some Cu-containing solid phase, interact with organic matter, form other soluble species, or change oxidation state if the oxidation–reduction (redox) conditions of the soil change. If any of these processes change the Cu^{2+} concentration, Cu bioavailability to plants will change.

The solubility and, as a consequence, the bioavailability of trace elements can be greatly influenced by soil pH. Generally, the bioavailability of the cationic metals will increase as soil pH decreases. Soil pH effects on the bioavailability of oxyanions are more variable. Arsenic, Mo, Se, and some forms of Cr often become more available as pH increases.

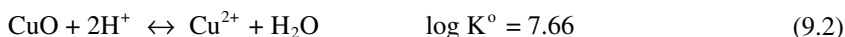
There are a number of reasons the bioavailability of trace elements is affected by changes in soil pH. Protons or hydroxyl ions can compete for adsorption or complexation sites and, therefore, a change in the activity of H^+ or OH^- can alter the partitioning of trace elements between the soil solution and the soil solids. A change in the soil solution pH can change the suite of trace element–containing soluble species. For example, at $pH < 6$, Pb^{2+} predominates while at pH 6 to 11, the $PbOH^+$ species predominates. Trace element solid phases can also have pH-dependent solubilities. In situations where these solid phases are controlling the solubility of a trace element, the bioavailability of the element will be influenced by changes in pH. A simple example is given below where the mineral tenorite (CuO) is dissolved by the addition of hydrogen ions. The equilibrium expression is also given along with an algebraic expression describing the changes in the logarithm of the Cu^{2+} activity with changes in pH. In deriving the last expression we have

Table 9.7 Concentrations (mg/kg) of Selected Elements in Alfalfa Tissue as Influenced by Soil pH

pH	Cd	Cu	Ni	Mo
6.0	0.8	17.7	1.9	193
7.0	0.6	16.8	0.8	342
7.7	0.4	16.0	0.8	370

Source: Pierzynski (1985).

assumed that the activities of H_2O and the solid mineral CuO are equal to one, taken the logarithm of the equilibrium expression, and converted $\log(\text{H}^+)$ to pH.



$$\frac{(\text{Cu}^{2+})(\text{H}_2\text{O})}{(\text{CuO})(\text{H}^+)^2} = 10^{7.66} \quad (9.3)$$

$$\log(\text{Cu}^{2+}) = 7.66 - 2\text{pH} \quad (9.4)$$

So as the pH decreases, the Cu^{2+} activity will increase, and vice versa.

Table 9.7 illustrates the influence of soil pH on Cd, Cu, Mo, and Ni concentrations in alfalfa tissue. The bioavailability of Cd, Cu, and Ni decreases with increasing pH, whereas the opposite is true for Mo.

As was discussed earlier, there is a significant amount of chemistry involved in trace element bioavailability for plants. In addition, there are soil physical and biological aspects to this issue as well. The soil physical component involves the propensity of some trace elements to diffuse through the soil toward the organism. This aspect of bioavailability is lost during routine batch extractions of soil where a relatively small amount of soil is shaken with a large volume of an extracting solution. Recently, the use of a technique called diffuse gradients in thin films (DGT) has been adapted to soil systems. Briefly, this technique deploys a cation exchange resin covered with a diffusive gel into the soil and provides a measure of the ability of the soil to supply trace elements to the resin, including both chemical and physical factors. Figure 9.7 shows the relationship between DGT results and Cu concentrations in plants across a wide variety of soils. In addition, this figure shows that there is a very poor relationship between the total Cu concentration in the soil and plant Cu and supports the concept of the need for a measure of Cu bioavailability.

Our discussion thus far has focused on plants and the soil solution. It is not hard to imagine that the bioavailability of trace elements to other organisms, such as earthworms or other soil invertebrates that are in intimate contact with the soil solution, would also be influenced by similar factors.

9.6.2 Humans

For the bioavailability of trace elements to humans a completely different environment must be considered. Risk assessments for some trace elements, such as As and Pb, typically identify direct ingestion of soil as the primary route of exposure. Young children (6 months to 6 years old) are usually the most susceptible to this exposure pathway because they and their toys are often in contact with the floor or the ground and they have a tendency to place their hands in their mouths. Most children ingest approximately 30 mg of soil per day but some can consume several grams of

soil per day. Children with an abnormal craving for nonfood substances are called *pica* children and are at greatest risk for exposure to trace elements in soils.

Once soil is consumed by the child, it enters the digestive system and the behavior of the trace elements in that environment becomes important for considering bioavailability of the elements. The stomach is very acidic under fasting conditions with a pH as low as 1.5. The pH rises to approximately 7.0 when food is consumed and as the food moves into the upper intestines. In addition, the digestive fluids contain salts and enzymes that are not normally found in a soil environment. In such a harsh environment, the possibility exists that trace elements sorbed to the solid phase may be released into the digestive fluids where they are available for absorption through the intestinal walls. The FIAM is again believed to hold under these conditions. Bioavailability is then related to the likelihood that the trace element will desorb or dissolve in the digestive system. This tendency may be either a kinetically controlled process or an equilibrium-controlled process. Kinetics may be important because the soil particles may not come to equilibrium with the digestive

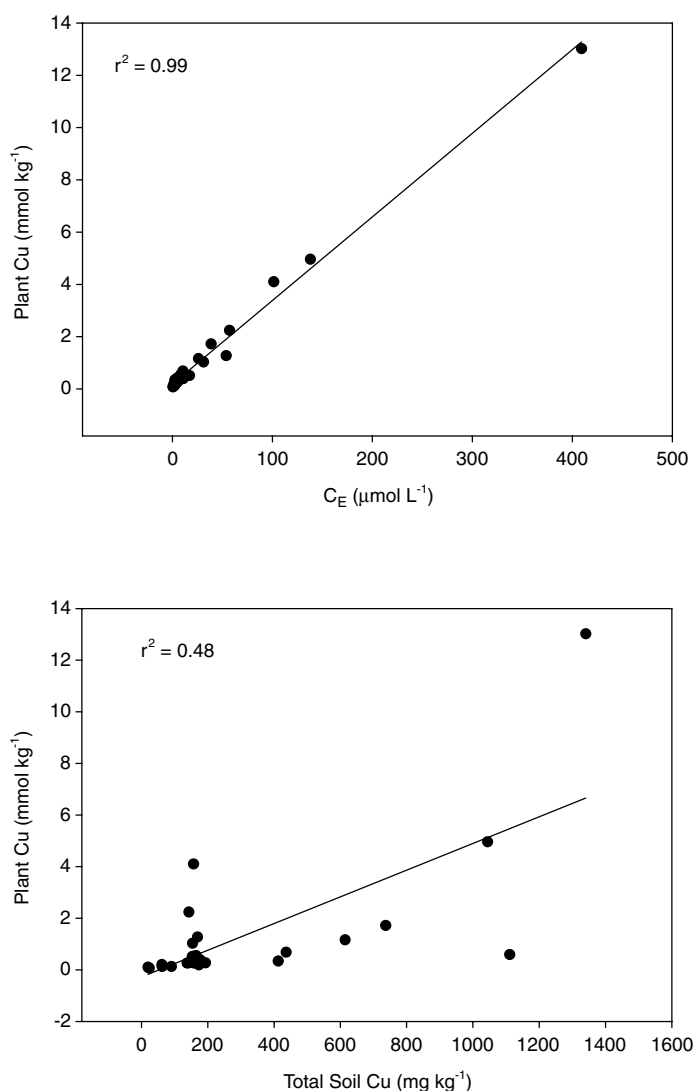


Figure 9.7 Total soil Cu concentration vs. a measure of Cu bioavailability (C_E) as a predictor of plant tissue Cu concentrations. (Data from Zhang et al., 2001.)

fluids in the time that they are present in the digestive system. In this case, a trace element that is released faster may have a higher bioavailability than one that is released more slowly. If desorption or dissolution is controlled by equilibrium conditions, then trace element bioavailability will increase with increasing solubility. As shown in Chapter 12, converting soil Pb to insoluble forms is one way to reduce bioavailability.

A considerable amount of research has been done in recent years addressing the question of measuring or estimating trace element bioavailability in soils. Two general approaches are to use an organism or to use an empirical estimate of bioavailability that correlates with the response of interest in an organism. The logic in using an organism is that the organism is the ideal indicator of bioavailability. Using an organism is not always practical, however, as it would be difficult to assess plant uptake of trace element for a large number of soils under field conditions or to use humans to assess bioavailability. In the case of human studies, surrogate species may be employed. Whenever vertebrate animals are involved in testing, cost becomes an issue. The empirical estimates generally involve a soil extraction and facilitate the evaluation of a large number of soils and can substitute for animal studies if the results are adequately correlated with the response of interest. When these surrogate tests are used, it would be more appropriate to describe the measured fraction as extractable or bioaccessible, because uptake by an organism is the only true way to assess bioavailability.

A combination of soil extractions and animal models has been used to assess soil Pb bioavailability. Table 9.8 shows the relative bioavailability of Pb from various Pb minerals and contaminated soils as determined by pig and rat feeding studies. Here the animals have been fed the Pb-contaminated materials in their regular diet and the amount of Pb that ends up in the blood, bone, liver, or kidney is used to estimate bioavailability compared with doses of Pb from Pb acetate, a soluble form of Pb, that give similar responses (hence, the name relative bioavailability). In this case galena (PbS), a form of Pb that is often mined, has a very low relative bioavailability while

Table 9.8 Relative Bioavailability of Lead, as Compared to Lead Acetate, in Galena (PbS), Paint, and Various Soils and Mine Waste Materials as Determined by Swine and Rat Feeding Studies, and Bioavailability as Determined by Human Dosing Studies

Pb Source	Test Organism	Relative Bioavailability as Determined by				
		Blood	Bone	Liver	Kidney	Ref.
Galena (PbS)	Swine	0.01	0.01	0.00	0.01	1
Leaded paint	Swine	0.82	0.63	0.85	0.70	2
Leadville, CO (soil)	Swine	0.71	0.62	0.92	0.92	3
Arkansas Valley, CO (mine waste)	Swine	0.20	0.18	0.11	0.10	3
Oregon Gulch (mine waste)	Swine	0.06	0.004	0.05	0.04	3
Butte, MT (soil)	Swine	0.22	0.13	0.09	0.13	4
Joplin, MO (soil)	Rat	0.34	0.34	0.27	0.48	5
Joplin, MO (soil and rock phosphate)	Rat	0.24	0.24	0.19	0.39	5
Bunker Hill, ID (soil)	Humans (fasting)	0.26	—	—	—	6
Bunker Hill, ID (soil)	Humans (fed)	0.03	—	—	—	6

Sources:

1. Casteel et al., 1998a.
2. Casteel et al., 1998b.
3. Casteel et al., 1998c.
4. Casteel et al., 1998d.
5. Hettiarachchi et al., 2003.
6. Maddaloni et al., 1998.

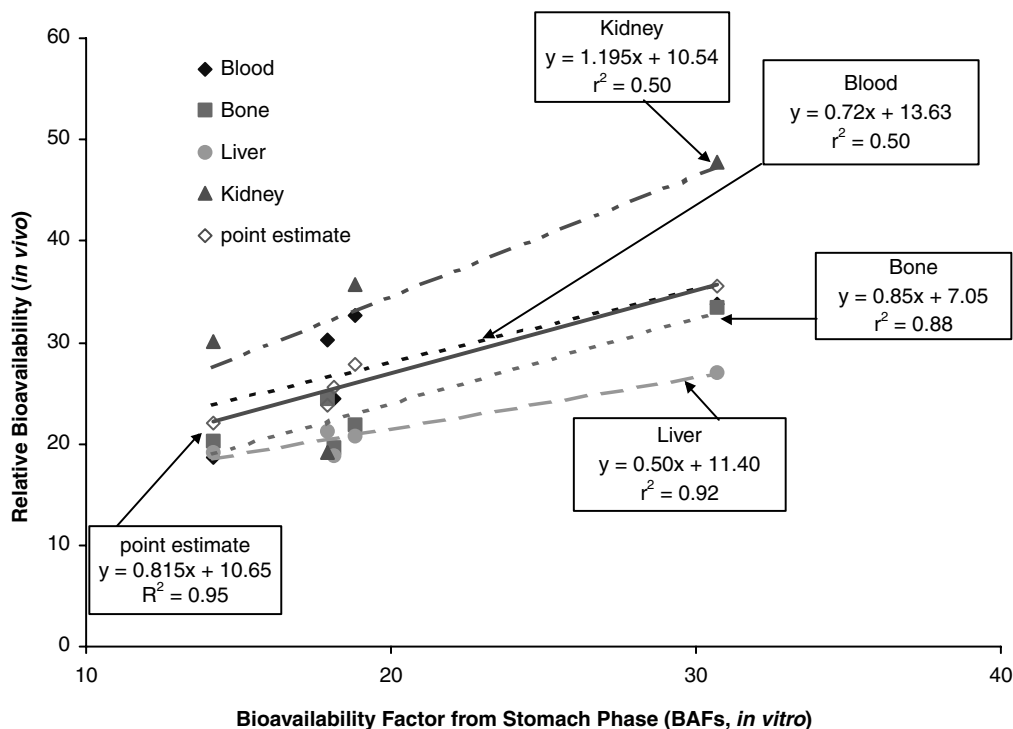


Figure 9.8 Relationship between soil Pb extracted with a simulated gastric solution and the relative bioavailability of the Pb as indicated by the physiological response of rats fed the same soil. (From Hettiarachchi, G. M. et al., *J. Environ. Qual.*, 32, 1335, 2003. With permission.)

the relative bioavailability from leaded paint is quite high. Lead bioavailability from the soils and mine waste varies considerably and the addition of rock phosphate to one soil reduced bioavailability. Figure 9.8 shows the relationship between soil Pb extracted with a simulated gastric solution (*in vitro*) and Pb uptake by rats (*in vivo*) that lends support to use empirical estimates of bioavailability in lieu of animal feeding trials. Also shown in Table 9.8 are data from human studies, which are quite unique. Test subjects were given a capsule of Pb-contaminated soil, either in a fasting condition or immediately after consuming a meal, and the ratio of two different stable isotopes (see Section 9.7) of Pb were monitored in blood for 30 h. The measurement of the isotope ratios allowed the investigators to calculate the amount of the administered dose that was absorbed by the test subjects. Lead consumed on an empty stomach is readily absorbed compared to that consumed with food. Generally, toxicological studies are not conducted using humans. This study was allowed to take place because the Pb dose administered would have kept the blood Pb concentrations of the subjects below 10 µg/dL even if the soil Pb had a bioavailability of 100%.

9.7 RADIONUCLIDES

The *radionuclides* include a wide variety of radioactive isotopes of elements that are the result of naturally occurring isotopes and our efforts to produce electricity with nuclear power, to develop and use nuclear weapons, and to use radionuclides in research and for medical purposes. Radionuclides might include various isotopes of americium (Am), cerium (Ce), Co, cesium (Cs), Fe, I, krypton (Kr), plutonium (Pu), radium (Ra), radon (Rn), ruthenium (Ru), thorium (Th), uranium (U), and Zn that are normally present in plants and soils at low concentrations and as such would be considered trace elements. In addition, there are elements such as barium (Ba), C, H, P, and S

that are typically present in high concentrations in soils or plants that would not be considered trace elements and that have radioactive isotopes. Regardless, because many of the concepts and concerns about radionuclides are unique, they are discussed separately — despite that most are trace elements — rather than trying to include these unique aspects into the previous sections. The environmental chemistry of the radionuclides is similar to that already discussed for trace elements. Radionuclides occur as cationic metals, oxyanions, and halides and the fate and transport processes will be the same. Bioavailability issues will also be similar, with the addition of the effects of radiation on organisms.

A brief explanation of some of the concepts of radionuclides is necessary for an understanding of the sources of the radionuclides and the potential environmental problems. Two parameters that are used to describe the nucleus of an atom are the *atomic number* and the *mass number*. The atomic number is the number of protons in the nucleus and this determines the identity of the element. The mass number is the sum of the protons and neutrons in the nucleus. A given element will have a set atomic number but different atoms can have varying mass numbers, meaning that the number of neutrons in the nucleus varies. This collection of nuclei is called the *isotopes* for that element, defined as having the same atomic number but varying mass numbers. The isotopes of an element are described by the system: ${}^N\text{X}$ where X is the elemental symbol and N is the mass number. For example, P, with an atomic number of 15, has the known isotopes of ${}^{28}\text{P}$, ${}^{29}\text{P}$, ${}^{30}\text{P}$, ${}^{31}\text{P}$, ${}^{32}\text{P}$, ${}^{33}\text{P}$, and ${}^{34}\text{P}$. The number of isotopes per element varies from H with 3 to Cs and xenon (Xe) with 36 each. Isotopes that do not undergo radioactive decay are called *stable isotopes*, and those that do decay are called *radionuclides*.

It would seem possible that an element could have a large number of isotopes because, at first glance, it would appear that any number of neutrons could be associated with a fixed number of protons. However, relatively few combinations are stable enough to persist in nature and the range of neutron-to-proton ratios for known isotopes is relatively narrow (0.5 to 3.0). This leads to a discussion of radioactive decay. Radioactive decay occurs when the ratio of neutrons to protons in the nucleus of an atom is such that the nucleus is unstable. Under these conditions the isotopes will undergo nuclear changes sooner or later such that the resulting nucleus is in a position of greater stability than the initial condition. Radioactive decay can be viewed as an adjustment of the neutron-to-proton ratio from a less to a more stable condition for the nucleus of an atom. There are numerous modes of decay that can generally be described as the conversion of neutrons to protons, the conversion of protons to neutrons, the combination of an electron and a proton to form a neutron, or the emission of an alpha particle which consists of two protons and two neutrons (elements of higher atomic number only). In each mode the neutron-to-proton ratio is changed by gaining or losing protons or neutrons, or by the loss of two protons and two neutrons. These changes are accompanied by the loss of other subatomic particles and energy in various forms. The emission of the subatomic particles and the energy is what makes the radionuclides both useful and dangerous.

A measure of the rate of radioactive decay of an element is its *half-life*. The half-life is the length of time required for half of the atoms to undergo radioactive decay. Each radioactive isotope has its own half-life, and the values can range from milliseconds to millions of years. The rate of radioactive decay is described with the unit of becquerel (Bq), which is defined as one decay per second. This unit is named after Henri Becquerel, a French scientist who discovered radioactivity in 1896. The rate of radioactive decay is also described with the unit of curie (Ci), defined as the rate of decay of 1 g of pure radium (${}^{226}\text{Ra}$), or 3.7×10^{10} disintegrations per second, and named after Marie Curie, who was a leader in the study of radioactive elements. Logically, $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$. To put this in perspective, an operating nuclear power plant would contain approximately $5.5 \times 10^{20} \text{ Bq}$ ($1.5 \times 10^{10} \text{ Ci}$); relatively concentrated radionuclides stored for research purposes would contain approximately $3.7 \times 10^8 \text{ Bq}$ (10 mCi); diluted radionuclides used in biological experiments would contain $3.7 \times 10^5 \text{ Bq}$ ($10 \mu\text{Ci}$); and the naturally occurring radioactivity in a 70-kg person from ${}^{40}\text{K}$ would be approximately 4440 Bq ($0.12 \mu\text{Ci}$). As an example, if we had $4.0 \times 10^6 \text{ Bq}$ of ${}^{90}\text{Sr}$ (half-life = 29 years), there would be $1.0 \times 10^6 \text{ Bq}$ after 58 years (two half-lives).

All elements that occur naturally today have at least one stable isotope or one isotope that has a very long half-life. A stable isotope is an isotope that does not undergo radioactive decay. Many elements have several stable isotopes. Phosphorus, used as an example previously, has seven isotopes but only one stable isotope (^{31}P). The remaining isotopes all have relatively short half-lives (<25 days) that have long since decayed so the natural abundance of ^{31}P is 100%. Iron, on the other hand, has ten isotopes, four of which are stable. The isotopes are ^{54}Fe , ^{56}Fe , ^{57}Fe , and ^{58}Fe with natural abundances of 5.8, 91.8, 2.1, and 0.3%, respectively.

9.7.1 Occurrence of Radionuclides

Radioactive elements are present for a variety of reasons. A number of primordial isotopes were present when Earth was formed. These isotopes obviously have long half-lives compared to the age of the Earth. Some of these isotopes decay to nonradioactive daughter products while others, such as the isotopes of U, decay to a series of radioactive daughter products. The decay scheme for ^{238}U , for example, has 14 radioactive daughter products with half-lives ranging from microseconds to thousands of years before the stable isotope ^{206}Pb is produced (Figure 9.9). The inert gas ^{222}Rn (radon) is one of the daughter products that has recently received attention as a hazard in the home when it builds up in the indoor air and is inhaled; this is discussed under environmental effects in Section 9.7.3. The Rn comes from the decay of U daughter products that are present in small amounts in the soil and rocks underneath the house.

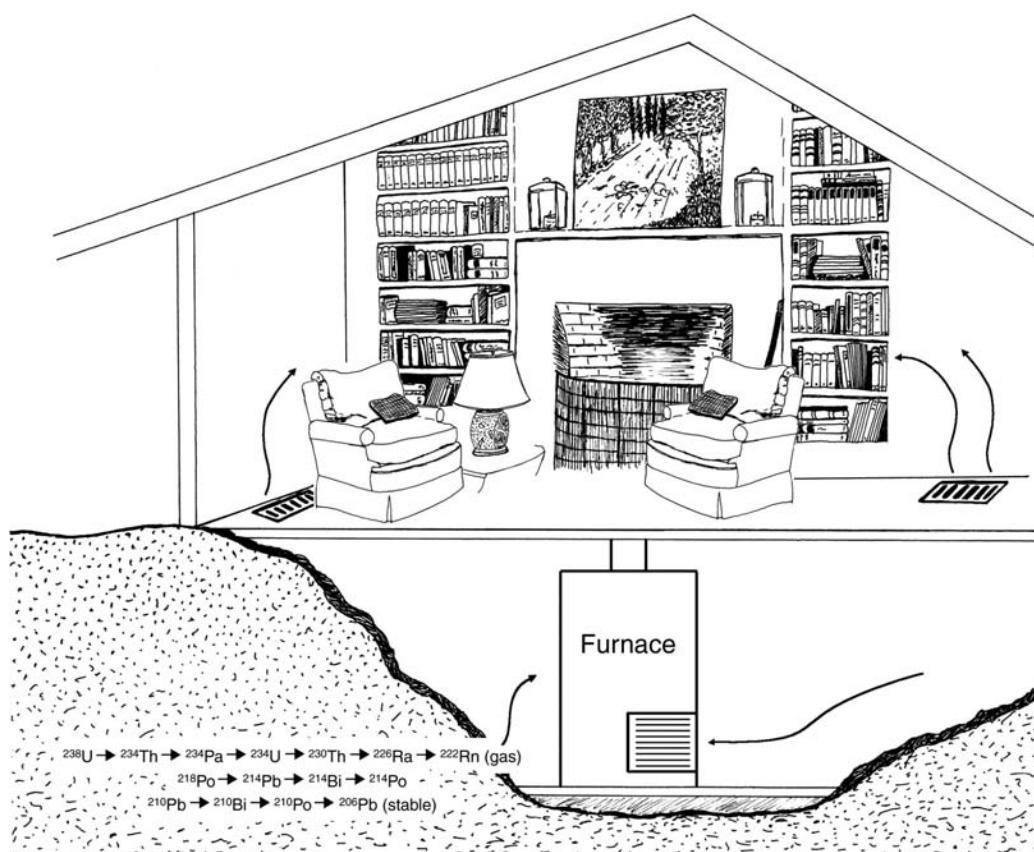


Figure 9.9 Production of Rn from radioactive decay of ^{238}U and possible entry pathways for a home basement. (Drawing by Sarah Blair.)

A fairly constant input of radionuclides from the atmosphere originates from the interaction of cosmic rays with air and other atmospheric constituents. One such important isotope is ^{14}C , which is often used for determining the age of organisms that have been dead for long periods of time. The atmosphere contains a fairly uniform amount of *cosmogenic* ^{14}C that is incorporated into living tissue — the uptake of carbon dioxide (CO_2) during photosynthesis, for example. When the organism dies, ^{14}C assimilation stops and the age of the organism can be estimated based on the initial amount of ^{14}C assumed to be present and the activity of ^{14}C remaining in the sample. This works if the organism is not too much older than the 5760-year half-life of ^{14}C .

The infrastructure associated with the nuclear power industry also concentrates and generates a significant quantity of radioactive materials. The mining of U for nuclear fuel poses a host of environmental and occupational problems ranging from worker safety to potential ecosystem exposure to radioactivity from dust and wastewater. Conditions inside the reactor are such that a variety of radionuclides are produced as daughter and fission products. *Fission products* are the result of splitting of nuclei to produce elements of lower atomic weight. Nearly 40 radioactive isotopes are present in an operating light-water nuclear reactor, although many of these have short half-lives and decay quickly when the reactor is shut down. When these daughter and fission products are contained, they pose no threat to the environment, but when accidentally released, as occurred in the Chernobyl nuclear accident in the former Soviet Union in 1986, they present significant risks to exposed individuals. Similarly, the infrastructure associated with the production, use, and testing of nuclear weapons concentrates and generates significant quantities of radioactive materials. Atmospheric fallout from aboveground testing of nuclear weapons has delivered low doses of radioactivity worldwide, and many of the facilities used in the development of the weapons are contaminated with radionuclides.

Finally, the use of radionuclides for research or medical purposes produces large quantities of radioactive materials. In research, radioactive isotopes are used to trace the path of elements through chemical reactions and biochemical processes. In medicine, radioactive isotopes are used for diagnostic and therapeutic purposes. Generally, the use of radionuclides in this capacity does not pose a significant threat to the environment, although the disposal of the resulting low-level radioactive waste has been a major issue for society.

Table 9.9 presents general information on a number of environmentally important isotopes. These isotopes are either naturally occurring and contribute to background radiation or have been released into the environment from anthropogenic activities and have been a concern from a human health perspective.

Table 9.9 Selected Environmentally Significant Radionuclides

Isotope	Half-Life	Principal Mode of Decay	Sources/Concerns
^{14}C	5760 years	Beta	Cosmogenic, nuclear reactors, and explosions
^{60}Co	5.27 years	Beta	Nuclear reactors and explosions
^{134}Cs	2.06 years	Beta	Nuclear reactors and explosions
^{137}Cs	30.1 years	Beta	Nuclear reactors and explosions
^3H	12.3 years	Beta	Nuclear reactors and explosions
^{131}I	8.1 days	Beta	Nuclear reactors and explosions
^{40}K	1.3×10^9 years	Beta	Ubiquitous, contributes to background radiation
^{222}Rn	3.8 days	Alpha	Inert gas that can build up in homes; contributes to background radiation
^{90}Sr	29 years	Beta	Nuclear reactors and explosions
^{235}U	7.1×10^8 years	Alpha	Used in nuclear weapons and reactors, source of Rn
^{238}U	4.5×10^6 years	Alpha	Used in nuclear weapons and reactors, source of Rn

9.7.2 Characterizing Radiation Dose

As there are numerous modes of decay for radioactive elements, there are also different types of nuclear radiation that can be produced. A single nucleus can decay and release more than one type of radiation. The most important types of radiation from an environmental standpoint are *alpha (α) particles*, *gamma (γ) rays*, *x-rays*, and positively or negatively charged *beta (β) particles*. Alpha particles are helium nuclei containing two neutrons and two protons that are emitted when some isotopes with a high atomic number decay. They are large particles that travel at a relatively low velocity. Gamma and x-rays are electromagnetic radiation of varying energies that travel at the speed of light. The emission of γ and x-rays does not change the number of neutrons or protons in a nucleus. Rather, these are generated when atoms release energy as a result of radioactive decay. Beta particles are small charged particles that travel at velocities near the speed of light.

A complete description of the methods for detecting radiation produced from radioactive decay is beyond the scope of this book. The methods depend on the type and energy of the radiation. Survey-type instruments, such as the Geiger counter, can be used to detect gross counts of nuclear disintegrations. More sophisticated methods are used in research applications or for environmental monitoring for the quantification of radioactivity from individual isotopes.

From an environmental standpoint we are interested in the effects of the nuclear radiation on organisms and how exposure occurs. In this case it is justified to focus on the human health aspects because some of the health effects, such as cancer, have long latency periods and are generally not a concern for other organisms. Acute radiation effects are quite rare and are associated with serious industrial accidents or nuclear war. Low-level chronic exposure over long periods of time is far more common. In both cases, the ability of the radiation to strip electrons from atoms and form ions in living tissue leads to much of the damage that occurs and is the basis of the name *ionizing radiation*. The ionization ruptures chemical bonds and disturbs normal cell functions. The number of cells that are disrupted, their functions, and the biochemical processes that are affected determine the overall effect on the whole organism.

The absorbed dose of radiation by living tissue is described with the units of *gray (Gy)* or *radiation absorbed dose (rad)*. The Gy is the preferred SI unit. These units characterize the amount of energy that is deposited in living tissue as radiation passes through; 1 Gy is equivalent to 10,000 ergs of energy deposited per gram of tissue and 1 rad is equivalent to 100 ergs of energy per gram (1 Gy = 100 rads). The effect of that absorption varies depending on the type of tissue and the energy or source of the radiation. For this reason, the rad or Gy is not used to characterize radiation effects. To do so, these additional factors are taken into account and the *equivalent dose* is used. The equivalent dose has the units of *sievert (Sv)* or *roentgen equivalent man (rem)*, which reflects the amount of energy dissipated in the tissue and the potential biological damage from that energy. The Sv is the preferred SI unit; 1 Sv is equivalent to 100 rem. For small doses the mSv is often used, where 1000 mSv = 1 Sv. The advantage of the equivalent dose is that a given dose will have the same effect regardless of the radiation source.

Whole-body exposure to 250 mSv in a short period of time can have measurable effects on white blood cell count, and 4000 mSv will result in death to half of the exposed population. Natural background radiation exposures are approximately 2 mSv/year from outdoor activities and 5 mSv/year from living in a brick house. A dental or chest x-ray film supplies 10 mSv per film. Allowable exposure levels for the whole body, head, and trunk are on the order of 50 mSv/year or 12.5 mSv for each 13-week period with higher exposures allowed if confined to the extremities. These levels are for workers who are occupationally exposed and should not be viewed as exposure guidelines for the general public. There are additional concerns for internal exposure. Internal exposure includes inhalation and ingestion of radionuclides in air, food, and water or absorption through the skin. In this case, all the energy from the isotopes may be dissipated within the body. In addition, some radionuclides are selectively concentrated within

the body. Examples include I in the thyroid gland and Ca, strontium (Sr), and P in the bones. From an environmental standpoint, internal exposure through food chain transfer or inhalation pathways is generally of greatest concern.

9.7.3 Environmental Effects

Significant environmental problems from radionuclides are the result of mining and processing of U ores and fuels for weapons and nuclear power plants, nuclear weapons detonations and testing, nuclear power plant accidents, and the occurrence of radon gas in homes. Some additional risk exists in storage facilities for nuclear wastes (including spent nuclear reactor fuels), but no significant problems have occurred in recent history. With the exception of radon gas, the locations of most of the contaminated sites are known and there is little exposure to the general public from radiation beyond normal background levels.

Any contamination resulting from U will involve a variety of radioactive isotopes. As shown in Figure 9.9, the decay scheme for ^{238}U has 14 radioactive daughter products. This isotope represents approximately 99.3% of the U in U ore. The balance of the U in the ore is generally ^{235}U , which produces nine radioactive daughter products before the stable isotope ^{207}Pb is formed. In addition, nuclear reactors and nuclear detonations produce a variety of other radioactive isotopes with varying half-lives. Some of greater significance include ^{137}Cs , ^{90}Sr , ^{131}I , and ^{129}I . The Cs and Sr isotopes have long half-lives and are the primary contaminants remaining after nuclear explosions and reactor accidents involving the core material. The I isotopes have short half-lives, but are concentrated in the thyroid gland.

Uranium mining activities are relatively small compared with mining activities for metals or coal so the potential area of impact is restricted. Mine worker exposure is the primary concern. Much of our knowledge related to radon exposure comes from data on U mine workers. Facilities involved with the processing of the ores, particularly the production of highly enriched materials for use in weapons and as reactor fuel, have created a number of highly contaminated sites. Early work with radioisotopes proceeded without much knowledge of the health effects from radiation exposure or an appreciation for the fate and transport of radionuclides in the environment. Radioactive wastes were often disposed of in open pits with resulting contamination to soil, sediment, and groundwater environments. Major facilities are located at the Savannah River Site in South Carolina, the Oak Ridge Site in Tennessee, Rocky Flats in Colorado, and the Fernald Feed Materials Production Center in Ohio. The elements of concern include radioactive isotopes of U, Ra, Rn, Th, Pu, and Cs as well as ^3H , ^{90}Sr , and ^{60}Co . Public access to these areas is restricted and public exposure to radiation hazards is essentially nonexistent. The Department of Energy is spending millions of dollars in cleanup efforts. Most of the remediation thus far has been either *in situ* stabilization or excavation and storage at approved waste disposal sites.

The most severe nuclear reactor accident occurred on April 16, 1986 at the Chernobyl nuclear power plant in the Ukraine. The combination of some safety systems for one reactor that had been turned off during an experiment and a number of safety violations allowed an explosion to occur that punctured the roof of the reactor building and exposed the reactor core to the atmosphere. Ensuing fires allowed radioactive elements to escape from the reactor until May 6 when liquid nitrogen was used to cool the reactor core. Approximately 3.5% of the reactor inventory was released as 16 different radioactive isotopes. From a human health perspective, the isotopes ^{131}I , ^{134}Cs , ^{137}Cs , and ^{90}Sr were the most important. The Soviet republics of Ukraine and Byelorussia were the most affected. Approximately 135,000 people were evacuated from within 30 km of the reactor. Outside the former Soviet Union, much of the fallout occurred north of the Chernobyl site in the Nordic countries. Sweden received approximately 5% of the fallout. Areas in Sweden received fallout of ^{137}Cs 100 times higher than that during atmospheric testing of nuclear weapons.

Of the 203 people diagnosed with acute radiation sickness, 31 died within a few weeks of the accident. People in the immediate vicinity received substantial quantities of ^{131}I , which accumulates in the thyroid gland and is expected to increase the incidence of thyroid cancer. Attempts were made to provide people with KI supplements to prevent uptake of ^{131}I by the gland, but they did not occur quickly enough to prevent all of the problems. Equivalent doses to people within 30 km of the reactor ranged from 4 to 3000 mSv.

Outside the former Soviet Union, scientists focused on the exposure of the general public to ^{137}Cs . Exposure could occur by external radiation from exposure of contaminated soils or other materials, inhalation of contaminated dust, or by consumption of contaminated food. Food chain transfer was considered to be a significant long-term threat and considerable efforts were made to minimize this risk. Tillage was recommended for soils to bury and dilute the radionuclides. Forage crops that were in the field during the fallout were not fed to animals. When the forages were cut, a higher cutting height than normal was recommended. Animals were kept out of pastures that had received fallout for some time afterward. Potassium fertilization was recommended because high K levels helped prevent ^{137}Cs uptake by plants. Overall, the highest radiation doses estimated for people outside the former Soviet Union for the year after the accident were approximately 7 mSv, which is more than the typical background dose, but less than what is believed to be the minimum dose to have health effects. The true health effects will not be known for a long time.

Several minor (by comparison to Chernobyl) nuclear reactor accidents have occurred in the United States. The most recent was the Three Mile Island Reactor near Harrisburg, PA in 1979 and is the only accident involving a reactor producing electricity for commercial purposes. Approximately 120,000 L of cooling water was released accidentally during an incident in which a partial reactor core meltdown occurred. Most of the radioactivity that was released was in the form of radioactive Kr and Xe gases so no widespread contamination of soils or vegetation occurred. Some ^{131}I was released and exposure was detectable in a few individuals. However, the maximum exposure to any individual was estimated at 1 mSv, considerably less than the annual dose from background radiation.

The occurrence of radioactive Rn gas in homes has received considerable attention in the last 10 years. Of our average annual dose of radiation, approximately 80% comes from natural sources and of that approximately 55% comes from Rn. Next to smoking, Rn is believed to be a significant contributor to lung cancer. The American Lung Association estimates that 87% of lung cancers are caused by smoking with an additional 12% attributed to Rn. As shown in Figure 9.9, ^{222}Rn is a daughter product from the decay of ^{238}U . The decay of ^{235}U also produces Rn as ^{219}Rn . Uranium is a minor constituent of the soil and rocks nearly everywhere, but is more prevalent in some areas. When Rn is produced it enters the basement or crawl space of homes, where it accumulates. The health effects of Rn are not actually caused by Rn itself. Radon is a relatively inert gas and nearly as much is exhaled as is inhaled so there is little accumulation in the lungs. The problems arise because both isotopes of Rn have short half-lives and decay to one of the isotopes of polonium (Po). Radon-222 decays to ^{218}Po , and ^{219}Rn decays to ^{215}Po . The Po atoms have an electrostatic charge that allows them to adsorb to dust particles in the air, which facilitates their transport around the home. Radon itself is a heavy gas that would remain close to the floor if left undisturbed.

Levels of Rn that can be found in homes vary tremendously from location to location and testing of individual homes is the only way to be certain if a problem exists and to what extent it occurs. For homes that are built on a slab or with a basement, remediation generally involves drawing air from beneath the slab or basement floor and exhausting it above the roof line. Systems can be either passive (rely on the draft created by the exhaust pipe) or active (using an electric fan). For homes with a crawl space, simple ventilation is often sufficient. Passive Rn mitigation is often incorporated into newly constructed homes. If, after testing, Rn levels are too high, the passive systems can easily be supplemented with an exhaust fan to further reduce Rn levels. It is not difficult to perform Rn mitigation on an existing home. Many communities and states require Rn testing as part of any real estate transaction.

Environmental Quality Issues/Events

Lead and Zinc Mining in the Tri-State Mining Region

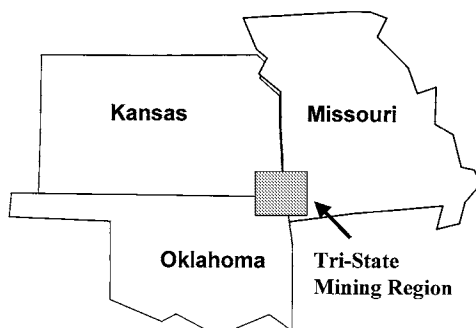


Figure 9.10 Map of Tri-State Mining Region.

As shown in Figure 9.10, the Tri-State Mining Region encompasses southeast Kansas, southwest Missouri, and northeast Oklahoma in the United States. Lead and Zn were mined extensively in this area for nearly 100 years beginning in the mid-1800s. The process of mining the ores and producing the final products of elemental Pb or Zn involved three steps: (1) the actual mining of the ores, with sphalerite (ZnS) and galena (PbS) the primary ores; (2) concentration of the ores; and (3) smelting of the concentrated ores. Early mining was generally done by excavating the ore from shallow pits, followed by crude concentrating and smelting techniques. Thousands of small operations dotted the landscape in the mining region. As mining techniques improved and the surface deposits were played out, shaft mining became the dominant method. Concentrating techniques also improved and fewer but larger smelters were used to process the ores. Most mining had ended by the 1950s with some smelting operations continuing into the 1970s.

The environmental problems from the Pb and Zn mining activities are widespread and complex. Ecological and human health risk assessments have indicated that Cd, Pb, and Zn are the primary contaminants of concern. In the areas where mining took place, the landscape is dominated by abandoned pits, shafts, smelters, and other equipment used in processing the ores, reflecting the range of technology that was used in the mining efforts, and representing direct safety threats to persons venturing onto the sites. A variety of waste materials are also evident. Chat was the first by-product produced from processing ore. It still has high concentrations of Cd, Pb, and Zn and is present in large quantities at different locations. Chat has found use as a construction material and consequently has been transported all over the region. Smelter slags are present in much lower quantities, but are highly enriched in metals. Smelters that were in operation most recently had tall smokestacks that emitted metal-enriched dust that was spread over large areas. One such smelter in Joplin, MO was surrounded by a residential neighborhood and created contaminated soils requiring remediation over 3 km from the stack. Because potential health effects of the contaminants of concern were not known until relatively recently, homes and schools have been built directly on or adjacent to mine wastes. These areas, plus those affected by smelter emissions, demonstrate the potential intimate contact between the contaminants of concern and the local population.

Depending on the location, mine shafts and pits often intersected shallow aquifers that were used as drinking water sources for individual homes. Surveys of water from these wells found that many exceeded the maximum contaminant levels (MCLs) for both Cd and Pb. Water samples from deeper aquifers had acceptable Cd and Pb concentrations.

Epidemiological studies have suggested that people living in or near the affected areas have higher incidences of chronic kidney disease, heart disease, skin cancer, and anemia compared with people living in nearby control areas. Surveys have found 10 to 20% of children 6 to 72 months old in some communities in the area have blood Pb concentrations higher than the maximum health guideline of 10 µg/dL. Human health risk assessments clearly demonstrate consumption of Cd above suggested guidelines (reference

doses) for both adults and children. Most of the risk came from consumption of locally grown food. Dermal contact with soil, ingestion of drinking water derived from shallow wells, and incidental ingestion of soil were also significant contributors. Data such as these provide evidence that genuine health problems exist and should be addressed.

The lack of vegetative growth on the mine spoils is direct evidence of ecological effects from the activities. This problem can be attributed to physical properties, low soil fertility, and to Zn phytotoxicity. The areas of exposed soil and mine wastes further exacerbate problems because they move metal-rich materials into sensitive environments and increases human exposure through windblown dust. Ecological risk assessments for terrestrial environments also indicate adverse effects on earthworms and other soil decomposers. Ecological risk assessments for aquatic habitats consistently show water and sediment contaminant concentrations exceeding benchmarks with observable impacts on aquatic invertebrate and fish communities.

Remediation efforts have been under way for some time, but are proceeding slowly. The region is divided into various subsites that are handled separately. Some of these subsites were placed on the Superfund National Priority List as early as 1985 while others may still need to be listed. The region covers portions of three states and two EPA regions, which creates some administrative challenges for prioritizing and funding the cleanup efforts. In general, remediation efforts involve addressing acute human health problems followed by chronic health problems and then possibly ecological problems. For example, to minimize Pb exposure in Joplin, MO, an emergency removal order allowed contaminated soil to be removed from around schools, playgrounds, day care centers, and other areas where children congregate. This was followed by soil removal from around homes with children known to have blood lead concentrations in excess of 10 $\mu\text{g}/\text{dL}$, soil removal from around homes with children, and then finally from around homes having soil exceeding 800 mg/kg Pb. In addition to soil removal, people were educated on how to reduce Pb exposure by proper cleaning of their homes, frequent hand washing, and maintaining proper vegetative cover in their yards. Homes using water from the shallow aquifer were supplied with an alternative water source, either bottled or from the public water system. Ecological problems have not received a great deal of attention yet; areas around Galena, KS were revegetated and recontoured in an attempt to stabilize large areas immediately around the city that were completely void of vegetation.

Preliminary results suggest treatment of acute health problems has been somewhat successful. Pb concentrations of children in Picher, OK that were originally high did decrease after their homes were remediated. Additional follow-up surveys will be required to determine definitively if the remediation efforts have been successful. Such surveys are 5 years after the remediation is complete. While to some the remediation efforts seem to be taking too long, people must realize that it took more than 100 years to create the problems and they will not be solved with just a few years of effort.

PROBLEMS

- 9.1 A poultry litter contains 600 mg/kg Cu, 500 mg/kg As, and 5 mg/kg Se. If the material is applied at 5 Mg/ha (dry-weight basis), calculate the application rates for Cu, Zn, As, and Se in kg/ha.
- 9.2 Using the average concentrations for As, Cd, and Pb given in Table 9.1, calculate the application rates for As, Cd, and Pb from the use of triple superphosphate, monoammonium phosphate, and diammonium phosphate supplying 40 kg P/ha.
- 9.3 Using the As application rate in Problems 9.2, determine how many applications of triple superphosphate would be required to equal the As from one application of poultry litter.
- 9.4 The top 30 cm of soil is contaminated and has 950 mg/kg Pb. Calculate the mass of Pb (in kg) in 1 ha of soil to the 30 cm depth. Assume a bulk density of the soil of 1.3 g/cm³.
- 9.5 List and describe at least five potential sources of trace elements for soils.
- 9.6 With 25 mL of a salt solution, 2 g of soil is extracted. The concentration of Cd in the extract is 0.1 mg Cd/L. In a separate analysis, 1 g of soil is completely digested in a small volume of strong acid. The digest solution is diluted to 50 mL and the concentration of Cd in the solution is 0.5 mg/L. Calculate the extractable and total Cd concentration of the soil in mg Cd/kg.

- 9.7 Describe the major adverse effects from high levels of trace elements in the environment. Be sure to link the effect with the element that causes the effect.
- 9.8 List five trace elements that occur as cations and five that occur as oxyanions in the soil solution. Use the elemental symbols and provide the valence for the cations. Use the molecular formula and provide the valence for the oxyanions.
- 9.9 Define bioavailability as it relates to trace elements in soils. Describe how bioavailability influences the potential adverse effects from trace elements in soils. Describe various approaches for estimating the bioavailability of soil trace elements.
- 9.10 Describe how factors that influence the bioavailability of trace elements in soils to plants might be similar or different from those that influence the bioavailability of trace elements in soils to humans after the soil has been ingested.
- 9.11 Assume a biosolids has As, Cd, and Pb concentrations as shown in Table 9.3, a potentially available N (PAN) concentration of 1.5%, and a total P concentration of 1.0%. Calculate the number of years that this biosolid could be applied before one of the cumulative load limits for As, Cd, or Pb shown in Table 9.2 is exceeded, first assuming that the biosolid is applied to supply 150 kg PAN/ha and then assuming the biosolid is applied to supply 30 kg P/ha. Which element is the land limiting constituent?
- 9.12 A soil contaminated with ^{137}Cs received 200 kBq/m² in nuclear fallout. Calculate the radioactivity 90 years later in kBq/m².
- 9.13 After the Chernobyl accident, plant uptake of ^{137}Cs was characterized by a transfer factor (TF) where:

$$\text{TF} = \frac{\text{Activity in plant dry matter (Bq/kg)}}{\text{Activity deposited (Bq/m}^2\text{)}}$$

An area in Sweden received an average fallout of 33 kBq/m². Grass grown in a pasture contained 680 Bq/kg prior to deep tillage (plowing) and 125 Bq/kg afterward. Calculate the TF before and after plowing to determine the effectiveness of this treatment for reducing ^{137}Cs uptake. (Data calculated from Rosen, 1996.)

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Organic Chemicals in the Environment

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10.1 INTRODUCTION

Modern society relies extensively on the use of organic chemicals for such needs as food additives, clothing, cosmetics, pharmaceuticals, and pesticides. Where would we be without organic chemicals that we use to clean our clothes (detergents, dry-cleaning solvents), power our vehicles (gasoline, diesel), heat our homes (natural gas, fuel oils, propane), or seal and protect our houses (asphalt shingles, paints, stains)? Just think of the numerous ways plastics, a diverse group of organic compounds, are used in everything around us. Because of the ubiquitous nature of organic chemicals, it is important that we understand the enormous role these materials play in our lives. In addition to gaining an appreciation and understanding of the benefits organic chemicals provide, we must also be aware of the hazards these materials present to human health and environmental quality when released into the environment.

The focus of this chapter is on organic chemicals in atmosphere, soil, and aquatic environments. Specific areas that are covered include sources and categories of organic chemicals; adverse effects of organic chemicals on human health and ecosystem quality; fate of organic chemicals in the environment; organic chemical analysis; and integrated and alternative pest management practices such as the use of biological control and genetically modified crops.

10.2 ORGANIC CHEMICALS

Organic chemicals are compounds that contain carbon (C) and usually at least one C–H (hydrogen) bond; C-based substances such as carbon monoxide (CO), carbon dioxide (CO₂), and carbonates (CO₃²⁻) are inorganic compounds. Over the last century millions of new organic chemicals have been developed. Thousands find their way into our daily lives even though many can be toxic if used or disposed of improperly. Therefore, it is imperative to understand the nature and behavior of organic chemicals in the environment, i.e., their impacts on different ecosystems and organisms, factors related to their mobility and fate, and evaluation of the type and quantities of various synthetic and indigenous organic substances.

The production of *synthetic organic chemicals* has increased rapidly since the beginning of the 1900s, with growth in the chemical industry resulting in new and improved materials that have affected the way we live. On average, more than 260 Tg (1 Tg = 10¹² g), or 286.5 million short tons, of C-based materials are manufactured annually in the United States. Organic compounds such as pesticides, lubricants, solvents, fuels, and propellants have great utility and are nearly indispensable in today's society. However, with the good comes the bad. Our heavy reliance on and use of organic compounds have also resulted in the unintended release of these substances into the atmosphere, hydrosphere, and soil environment, affecting both flora and fauna. More than 70,000 synthetic chemicals are used daily, most of which are organic chemicals. Human activity has contributed to the release of enormous amounts of these organic chemicals into the environment every day. *Petroleum products* are the dominant source of hydrocarbons released into the atmosphere due to human activities, with nearly 50% related to gasoline emissions. Contamination of groundwaters is receiving much attention; however, assessing the magnitude of the problem will be difficult unless the contaminant sources can be identified and prevented from further contaminating the environment.

10.2.1 Sources

The introduction of organic chemicals into the environment can occur by design, accident, or neglect. A variety of sources can contribute to the release of organic chemicals; industrial sites typically manufacture, store, and distribute the greatest amount of organic chemicals and therefore have a higher probability of contaminating the environment. Several *industrial sites* with the potential for contaminating our air, water, and soil environments are listed in Table 10.1. Other

Table 10.1 Some Examples of Industrial Sites with the Potential for Contaminating the Environment

Acid/alkali plant factories	Pesticide manufacture sites
Asbestos plants	Pharmaceutical, perfumes, cosmetics, toiletry factories
Chemical and allied products	Polymers and coatings operations
Explosives and munitions	Railway yards
Fertilizer/pesticide dealers	Rotogravure plants
Gas works and storage	Sewage treatment plants
Metal treatment and finishing	Shipping docks
Mining and extractive industries	Smelting and refining factories
Oil production facilities	Tanning operations
Oil storage sites	Waste disposal sites
Paint processing plants	Wood preservation facilities

sources that may be a cause for concern include land application of wastes, *concentrated animal feeding operations* (CAFOs), improper pesticide use, landfills, and oil or gas operations. Although the quality of groundwater is influenced by natural processes, as well as human activities, organic chemical contamination is generally a consequence of improper management by humans. As an example, creosote from a railroad tie operation has resulted in contamination of surface water and groundwater, which, as described in the Environmental Quality Issues/Events Box: Rehabilitation of a Contaminated Wood-Preservative Site (p. 396), can be difficult to remediate. More information on the remediation of organic-contaminated soils and waters can be found in Chapter 12.

10.2.2 Categories

Organic chemicals can be broadly classified as *aliphatic* (straight-chain), *aromatic* (closed ring with double bonded C), or combinations of aliphatic and aromatic, depending on their structural configuration (Figure 10.1). Many of these compounds also contain oxygen (O), nitrogen (N), phosphorus (P), sulfur (S) and halides, e.g., fluorine (F), chlorine (Cl), iodine (I), which impart specific qualities to organic substances that can make them extremely useful. However, some of these organic chemicals are highly toxic and hazardous to human health and the environment. Several industrial organic chemicals can be categorized as solvents, preservatives, petroleum products, refrigerants, explosives, polymers, and pesticides, which are some of the products of most benefit as well as concern in today's society.

Hydrocarbons, for example, comprise C and H linked together to form *alkanes* (contain only single-bonded C linkages), *alkenes* (contain double-bonded C linkages), *alkynes* (contain triple-bonded C linkages), *alicyclic* (single-bonded, cyclic C), and *aryl* (aromatic C) compounds. Hydrocarbons are generally considered to be of most environmental interest due to the great number of organic chemicals with these structures and their potential toxicity (e.g., ability to bioaccumulate in fatty tissue). Alkanes comprise some of the simplest hydrocarbons in that they contain single bonded C (C–C) and/or H such as methane (CH₄), ethane (C₂H₆), propane (C₃H₈), with other unbranched alkane formulas of C_xH_{2x+2}, where x represents the number of C atoms. Alkenes contain at least one double-bonded pair of C atoms (C=C) and include compounds such as ethene (C₂H₄) and propene (CH₂=CH–CH₃), as well as chlorinated substances such as trichloroethylene (CCl₂=CHCl) and tetrachloroethene (CCl₂=CCl₂). Alkyne compounds have one or more C-pair of triple bonds (C≡C); few of these compounds exist as pollutants. Acetylene (CH≡CH) has the simplest alkyne structure, is highly reactive, and when burned in an oxygen stream produces temperatures in excess of 3000°C (oxyacetylene torch). Another example of a triple-bonded compound would be the cyanides (C≡N[–]), which are highly toxic chemicals that can be found in and around gold (Au) heap leaching operations. Alicyclic hydrocarbons contain single-bonded, C-to-C structures such as cyclopropane (C₃H₆) and cyclohexane (C₆H₁₂). *Aromatic compounds* are a large and important group of hydrocarbons comprising ring structures that contain double-bonded

C pairs, which have a significant influence on the stability of these compounds. The simplest aromatic member is benzene (C_6H_6), one of the most common and stable organic chemical structures. Examples of these and more organic chemical structures are shown in Figure 10.1.

Although it is important to identify the type of C and H structural characteristics of organic chemicals, the presence of other elements (e.g., O, N, S, P, and the halogens) increase both the diversity and reactivity of organic chemicals. *Functional groups* comprise common elemental groups (see Table 10.2), which are constituents that give organic chemicals unique properties. How organic chemicals react in the environment is often dictated by the type of functional groups (or moieties) they contain. For example, oxygen-containing functional groups, which tend to be prevalent on

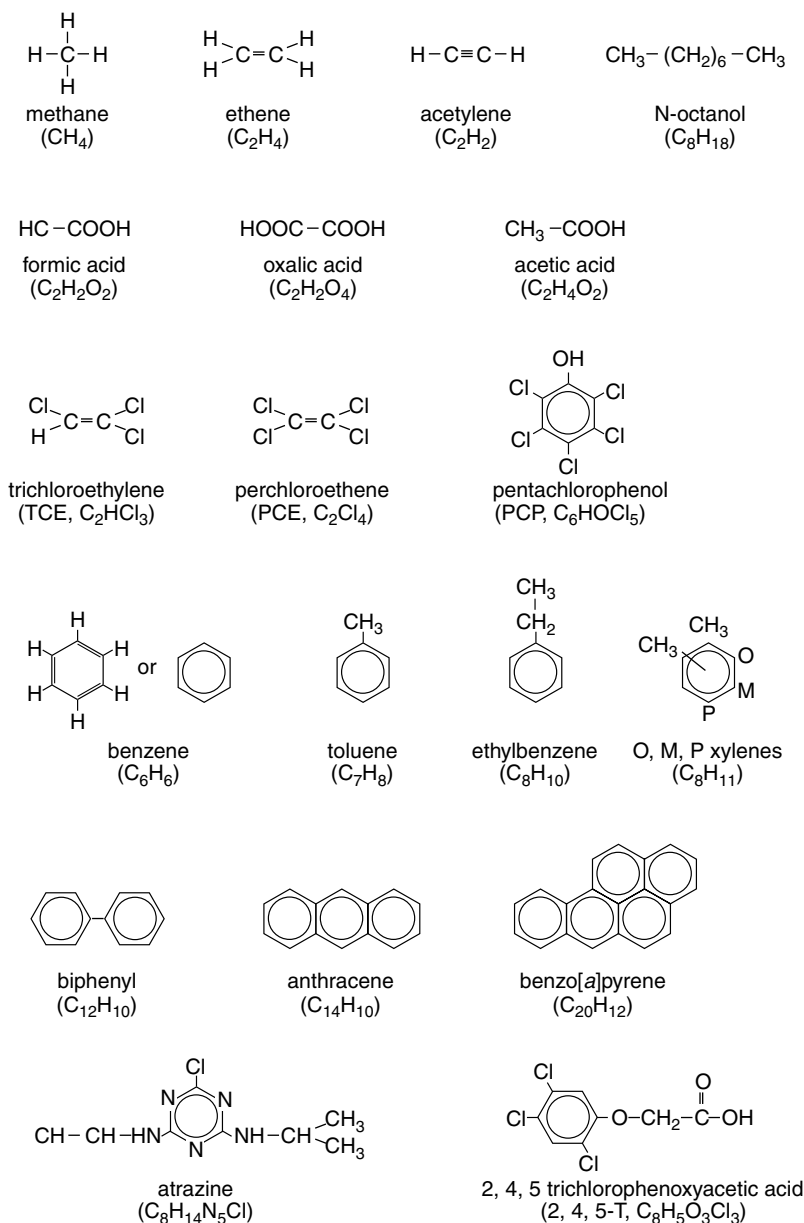
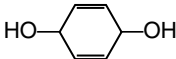
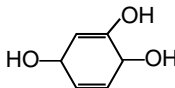


Figure 10.1 Example structures for common and hazardous organic chemicals.

Table 10.2 Examples of Functional Groups Containing Common Elemental Constituents That Give Organic Chemicals Unique Properties

Oxygen-Containing Groups			
alcohol	$R-CH_2OH$	aldehyde	$R-\overset{\overset{O}{\parallel}}{C}-H$
anhydride	$R_1-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R_2$	methyl	$R-CH_3$
carboxyl	$R-\overset{\overset{O}{\parallel}}{C}-OH$	carbonyl	$R_1-\overset{\overset{O}{\parallel}}{C}-R_2$
ether	R_1-O-R_2	ester	$R_1-\overset{\overset{O}{\parallel}}{C}-O-R_2$
hydroxy	$R-OH$	enol	$R-\overset{\overset{H}{\mid}}{C}=\overset{\overset{H}{\mid}}{C}-OH$
keto acid	$R-\overset{\overset{O}{\parallel}}{C}-COOH$	unsaturated carbonyl	$\overset{\overset{H}{\mid}}{C}=\overset{\overset{H}{\mid}}{C}-\overset{\overset{O}{\parallel}}{C}-H$
quinone		hydroquinone	
Nitrogen-Containing Groups			
amino	$R-NH_2$	imino	$R=NH$
amide	$R-\overset{\overset{O}{\parallel}}{C}-NH_2$	amine	$R-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-NH_2$
cyano	$R-C\equiv N$	nitro	$R-\overset{\overset{O}{\parallel}}{N^+}-O^-$
nitroso	$R-N=O$	nitroso	$R_1-\overset{\overset{NH_2}{\mid}}{\underset{\underset{H}{\mid}}{C}}-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{H}{\mid}}{N}-\overset{\overset{COOH}{\mid}}{\underset{\underset{H}{\mid}}{C}}-R_2$
Sulfur-Containing Groups			
sulfide	R_1-S-R_2	mercapto	$R-SH$
thioester	$R-\overset{\overset{O}{\parallel}}{C}-S-H$	ester sulfate	$R-O-SO_3H$

both natural and synthetic organic chemicals, can be protonated or deprotonated depending on soil or solution pH. Therefore, the *acidity* and *basicity* of the functional groups determine how an organic chemical may respond in the environment. In addition, *molecular size* and *shape* are characteristics that relate to the potential movement of an organic chemical in aquatic and soil ecosystems. The *polarity*, *polarizability*, and *charge properties* of an organic chemical are also significant factors in their interaction with environmental substances and organisms.

10.2.2.1 Petroleum Products, Solvents, and Industrial Synthetic Organics

Organic chemicals, particularly the hydrocarbons, have many uses. Alkanes with one to four C atoms are gases; those alkanes with five or more C atoms are liquids or solids under ordinary

conditions. Methane, a natural gas of immense importance to society as well as an environmental concern due to its increased levels in the atmosphere, has been implicated in global climate change (see Chapter 11). The chlorinated alkenes *trichloroethylene* (TCE) and *tetrachloroethene* (PCE) are used primarily as solvents. TCE and PCE have been extensively used or stored at military installations (e.g., missile silos, underground storage tanks, solvent cleaning facilities) and in the dry-cleaning industry to remove grease, oil, and other stains from clothing. TCE is a liquid under typical environmental conditions, slightly volatile, density greater than water (1.46 g/cm³), and is one of the most commonly encountered environmental contaminants. Because TCE has been identified in one third of U.S. groundwater supplies and is the primary source of contamination at most Superfund sites, there has been increasing interest in restricting the use of TCE and in remediating soils and groundwaters contaminated by TCE; release of TCE in the atmosphere also contributes to photochemical smog.

Petroleum products contain the *BTEX aromatic hydrocarbons* benzene, toluene, ethylbenzene, and xylenes (*o*-, *m*-, and *p*-xylenes), as well as alkanes and polynuclear aromatic hydrocarbons (PAHs). Combined, these substances represent some of the most prevalent contaminants of soils, sediments, and waters. Recently, the EPA identified 436,494 *leaking underground storage tanks* (LUST) that have resulted in environmental contamination of groundwaters with gasoline, petroleum products, and various industrial organics. As of March 2003, corrective actions have resulted in the cleanup of approximately 300,000 LUST sites. The EPA has identified BTEX compounds among the nine most common pollutants in relation to frequency of occurrence.

PAHs are derived from the incomplete combustion of hydrocarbon chemicals such as fossil fuels, smoke from wood-burning stoves, fireplaces, and cigarettes, and fuel in barbeque grills. They are also present in high concentrations in road and roofing asphalts comprised of coal tars and petroleum residues. In the incomplete combustion of aromatic compounds, more H is consumed than C, which results in larger, condensed aromatic ring structures. Therefore, PAHs are commonly produced, with significant amounts distributed in our air, soil, water, and food resources. Some of these materials are potential precursors (e.g., benzo[*a*]pyrene) of carcinogens and mutagens (see Chapter 13 for more information on these types of substances).

Another group of organic chemicals that has polluted the environment are the *polychlorinated biphenyls* (PCBs) (see Figure 10.1 for an example of a biphenyl compound). Commercial mixtures of PCBs, called aroclors, are distinguished by their chlorine content, which give them unique physical–chemical properties. Aroclors may consist of oily liquids to waxy solids with unique characteristics such as nonflammability, chemical stability, high boiling points, and electrical insulating properties. PCBs were used extensively in numerous industrial and commercial applications such as electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, and carbonless copy paper. Because of the toxicity and persistence of many pollutants, the U.S. Congress in 1976 enacted the *Toxic Substances Control Act* (TSCA), which prohibited the manufacture, processing, and distribution of several organic compounds including PCBs. The TSCA legislated “cradle to grave” (i.e., from manufacture to disposal) management of PCBs. Before PCB production was terminated in 1977, close to 1 Tg (1 million metric tonnes; a metric tonne = 1000 kg or 1 Mg) of PCBs were manufactured in the United States. One of the primary reasons for elimination of PCBs was due to their detection and bioaccumulation in fatty tissues of fish and marine mammals, as well as in humans. The U.S. Food and Drug Administration (FDA) has set an advisory limit of 2.0 mg PCBs per kg in commercially traded fish. Bioaccumulation of PCBs and other organic chemicals is due to the hydrophobic nature of the compounds, which makes them fat soluble.

10.2.2.2 Pesticides

Pesticides are classified according to the target organisms they are designed to control (Table 10.3). Of the target organisms, weeds cause the most significant economic loss due to their

Table 10.3 Categories of Pesticides Used to Control Unwanted Pests

Pesticide	Control
Herbicide	Prevents the growth of weeds in agricultural crops, lawns, golf courses, or is applied directly to weeds that are established
Insecticide	Kills or controls harmful or undesirable insects that live on plants, in animals, or in buildings
Fungicide	Protects plants from infestations by diseases; usually used prior to conditions that are favorable to disease development
Bactericide	Controls bacteria that can cause damage to fruit and develop galls on plants
Nematicide	Protects young plant roots from microscopic soil worms that infect plants and feed upon their roots
Acaricide	Controls mites and spiders that can infest or damage agricultural crops or ornamental plants
Rodenticide	Kills mice and rats living in homes and other buildings and prevents infestations or losses of food products in storage

interference with crop production. It is not surprising, therefore, that herbicides are the most commonly used pesticides, comprising more than 45% of the pesticides applied in the United States every year. Insects are the next greatest problem, with insecticide use totaling approximately 10% of the pesticides applied annually in the United States. Fungicides are the third most commonly used pesticides, totaling about 6% of U.S. pesticide consumption. Other pesticide use in 2001 amounted to approximately 40%. During this same year, worldwide market estimates were 36% herbicides, 25% insecticides, 10% fungicides and 29% others. In the United States alone there are approximately 0.56 Tg (0.56 million Mg) of pesticides (active ingredients) used annually, most of which are applied to control weeds, insects, and diseases, and to improve crop production. An estimated 25,000 Mg of pesticides are also used in nonagricultural applications such as pest control in lawns, flowerbeds, golf courses, forests, and in and along waterway, utility, and rail easements. Worldwide use of pesticides in 2001 was more than four times greater than in the United States at 2.4 Tg.

Environmental Quality Issues/Events

Process Involved in the Registration of a New Pesticide

Pesticides were first regulated in 1947 by the *Federal Insecticide, Fungicide, and Rodenticide Act* (FIFRA), which authorized the U.S. Department of Agriculture to oversee pesticide use. In 1954, the *Federal Food, Drug and Cosmetic Act* (FFDCA) authorized the FDA to regulate pesticides in food products. Administration of pesticide regulation and registration was assigned to the EPA in the early 1970s. All pesticides must now undergo an extensive process to be produced for commercial use. As many as 142 tests must be performed before a pesticide receives an EPA product label registration. These tests include comprehensive health, safety, and environmental evaluations that can typically take 8 to 10 years and cost up to \$50 million per pesticide.

Initially, an organic chemical proposed to be used as a pesticide is manufactured in small amounts to be tested in laboratory and possibly greenhouse studies that determine its ability to control pests, i.e., “biological activity” or “efficacy.” When biological activity is sufficiently demonstrated, the organic chemical is evaluated for its toxicity to laboratory animals and potential for causing genetic damage. Those pesticides that will be used for crop protection and that have met efficacy and safety standards are then tested in field studies. Field studies determine the appropriate rates and methods of application under valid conditions for crop production. Environmental behavior is also evaluated to examine the potential translocation, transformation, and persistence of the pesticide tested.

A decision to continue the development of a new pesticide comes after the initial few years of testing, which determine if there is a scientific and economic basis for commercializing the product. Millions of dollars and an extensive time commitment are required to continue testing the chemical properties, human and environmental concerns, prospective markets, efficacy, patent rights, manufacturing technology, and production costs of the potential pesticide. The EPA requires that considerable work be performed to verify the overall safety of the pesticide, which includes potential risks to the user, crop, environment, and consumers. *Product labels* must contain information on proper application methods, dosage, and particular safety issues such as protective clothing, training, specific hazards, time requirements related to human exposure of treated fields, environmental warnings, and container disposal.

Once a potential organic chemical is considered acceptable for further testing, the manufacturer must conduct numerous long-term studies before the EPA will grant a product label registration. There are six general areas of testing. *Product chemistry testing* includes evaluating the active ingredients and composition of the finished formulated product. *Toxicology testing* in animals must determine the acute effects of single doses, chronic effects of long-term or lifetime exposures, effects on reproduction, mutagenic effects on genes and inherited traits, and potential carcinogenic effects from lifetime exposure. In addition, the possibility of *pesticide residues* in food and feed products must be evaluated by testing raw crops, processed food, and animal feed, meat, milk, poultry, and eggs. *Environmental concerns* are evaluated by researching pesticide transformations in soils, waters, and different plants, and potential translocation by runoff, leaching, and spray drift. *Ecological effects* to birds and fish must be assayed to ascertain potential acute and chronic toxicity impacts, and short- and long-term effects to nontarget plants must be characterized. Finally, determining *pesticide efficacy* under a wide variety of conditions is required.

Before registering a pesticide, the manufacturer must apply for an *experimental use permit* (EUP) from the EPA to conduct large-scale field testing. Previous results from chemical, toxicological, environmental, and ecological tests will be assessed by the EPA before issuing an EUP. Residue tolerance levels must be determined by the EPA if the pesticide-treated crop materials are to be used for animal or human consumption, and, if tolerance limits cannot be determined, all exposed material must be destroyed. Because small amounts of pesticide residue are common in treated crops, large-scale product testing must be able to quantify the tolerance level of residual materials. These tolerance levels determine the maximum pesticide residues in foods for human consumption as well as animal feed that will be allowable by law. Additional safety margins are established by the EPA so that the residual pesticide limits will be safe to consumers.

Residual tolerances are established by the EPA as authorized by the FFDCA. The manufacturer of a pesticide must present evidence to the EPA that establishes the residue levels are safe. Safety margins defined for a potential pesticide must be determined by scientific methods that can detect the original pesticide and its metabolic products. All methods used by the manufacturer to evaluate residual compounds must be further verified by government laboratories before tolerance levels are officially certified. Although pesticide tolerances in food and feed supplies are enforced by the FDA, it is the responsibility of the USDA to monitor meat, dairy, and poultry products for pesticide residues.

Risk assessment is also required for all new pesticides. Calculations that are used in the risk assessment process must be as accurate and precise as possible so that assumptions related to different scenarios are sufficiently sound. Therefore, it is important to know the types of hazards and the extent of exposure associated with a pesticide. Studies conducted on the toxicological effects can be used to determine hazard potentials, and research involving pesticide characteristics and residue products facilitates the level of exposure related to the pesticide. Experiments such as feeding studies conducted on animals can be used to determine the *no observable effect level* (NOEL) for consumable materials. As an additional safety measure, the NOEL is divided by a factor (e.g., 100 or 1000) to determine a *reference dose* (RfD) or *acceptable daily intake* (ADI) level. These values represent the maximum amount of the pesticide residue that should be ingested by an average person over a day or lifetime so that harmful effects do not occur. See Chapter 13 for more information on risk assessment.

After all the studies, calculations, and assessments are completed, and the pesticide product is deemed useful and safe, the EPA is given the multitude of information developed for registering the organic chemical as a pesticide. The registration packet material contains volumes of information that must be reviewed, verified, and approved by the scientific and administrative branches of the EPA *Office of Pesticide Programs* (OPP). After the pesticide label is approved by the EPA, commercial

production and distribution for sale can proceed. The pesticide label is a legal document that provides information to the user as well as special precautions that protect consumers and the environment. Noncompliance with pesticide label directions is a federal violation that can result in civil and criminal penalties to violators.

10.2.2.3 *Pharmaceuticals, Personal Care Products, and Endocrine Disruptors*

Pharmaceuticals (e.g., drugs), personal care products, and endocrine disruptors are emerging groups of potential hazardous organic chemicals in the environment (Jones et al., 2002; Radosevich and Rhine, 2002). Most of these substances are released into the environment through disposal of animal and human wastes, animal confinement discharges, applications of pesticides, or as releases of synthetic organic chemicals. Combined, these organic chemicals comprise an extremely large and diverse group of substances that can invoke subtle responses as well as acute effects on nontargeted and indigenous organisms. Long-term exposure to low concentrations of these substances may invoke microbial resistance (a concern for antibiotics) and may induce allergic reactions in sensitive individuals.

Pharmaceuticals and personal care products (PPCPs) comprise a very broad, diverse collection of thousands of organic substances that are products used for human and animal health or for cosmetic purposes. Included in this group of organic compounds are human and veterinary *drugs*, *cosmetics*, *fragrances*, *sunscreen agents*, *biopharmaceuticals*, *diagnostic agents*, *nutraceuticals* (bioactive food supplements), and *excipients* (various inert substances used in PPCP manufacturing and formulation). Currently, more emphasis is placed on understanding pharmaceuticals than on personal care products because drugs are designed to be long-lasting and to maintain their chemical integrity in order to be therapeutically effective. Thus, the following discussion emphasizes pharmaceuticals, but in time personal care products may require great attention if significant environment impacts are discovered.

Unmetabolized pharmaceutical substances are excreted in urine and feces. Excreted pharmaceutical drugs and their derivatives can potentially pass through municipal sewage treatment facilities because these facilities were not designed to remove exotic anthropogenic chemicals. As a result of many years of land application of municipal biosolids, concentrations of pharmaceutical substances and their derivatives may have increased in the environment. While many of these substances, for example, antibiotics, are used in similar amounts as some agrochemicals and known organic pollutants, pharmaceuticals are not subjected to the same level of testing for possible environmental effects (see Environmental Quality Issues/Events Box: Process Involved in the Registration of a New Pesticide, p. 369). Agrochemicals also are used on a seasonal basis, whereas PPCP compounds can enter the environment continually through wastewater treatment facility discharges and their by-products. Several of these chemicals and their derivatives can be persistent, but even PPCPs that are short-lived may result in chronic exposures because of their continual release into the environment.

A significant amount of human *pharmaceuticals* that reach the environment is from hospitals, medical centers, and through disposal of discarded drugs. Various types of pharmaceutical compounds detected in wastewater treatment plant effluents and surface waters include *analgesics* and *blood lipid regulators*, *vasodilators* (enlarges blood vessels), and *anti-inflammatory* and *antiepileptic drugs*. PPCPs can also enter the environment through a variety of means in addition to sources derived from biosolid and effluent treatment discharges, including leachates from landfills, runoff from CAFOs, direct discharges from residential areas, through recreational activities, disposal of medicated animal excreta, and even discharges from cruise ships. CAFOs are known to be a major source of antibiotics and possibly steroids. A wide variety of PPCPs and their derivatives that are

disposed of into our wastewater system have been found in environmental samples including surface water and groundwater, and even in treated drinking waters.

Endocrine disruptors are another emerging group of environmental contaminants that are capable of having an impact on animal and human endocrine systems. Animal and human development is controlled largely by the *hormone system*, also known as the endocrine system, that signals growth, sexual development, and many other essential functions. The hormone system includes such organs as the testicles and ovaries and the thyroid, pituitary, and adrenal glands. These glands regulate biological processes that control growth and function of reproductive systems, regulation of metabolism, maturation of brain and nervous systems, and an organism's development throughout its lifetime. Endocrine disruptors, many of which are also pharmaceuticals, are *synthetic chemicals* that can mimic natural hormones by blocking cell receptor sites or trigger actions, thus modifying the natural growth and development of animals and humans (Damstra et al., 2002).

There are many chemicals used in today's society that are potential endocrine disruptors. For example, PCBs, dioxins, dichlorodiphenyltrichloroethane (DDT), and several pesticides are just a few of the known chemicals that can elicit endocrine responses (see Table 10.4). As mentioned earlier, manufacturing and use of PCBs (and also DDT) have been discontinued in the United States since the 1970s; however, these chemicals are still used in other countries. Even *common household items* — detergents, cosmetics, household cleaners, and plastic food containers — contain endocrine-disrupting chemicals that include *phthalates*, *alkylphenol*, and *ethoxylates*. Most of the endocrine disruptors identified in the environment are pesticides and their derivatives. Even though pesticides undergo an extensive process to become registered for commercial use, there is still much uncertainty surrounding their role as endocrine disruptors in the environment. This is because there is little testing of the risks associated with a pesticide's ability to act as an endocrine disruptor. Although some endocrine-disrupting chemicals can be persistent in the environment due to slow degradation and bioaccumulation processes, major concerns include enhanced food chain transfer, increasing levels in certain organisms, and possible synergistic effects associated with multiple endocrine disruptors. The normal pathway for introduction of endocrine disruptors is through consumption of

Table 10.4 Various Agents Known to Have Endocrine-Disrupting Capabilities

Endocrine Disruptor	Designated Uses
Alkylphenols	Domestic detergents
Bisphenol A	Dental lacquers; food can coating
Brominated flame retardants	Plastics and textiles
Butylated hydroxyanisole (BHA)	Food antioxidant
Parabens	Preservatives in cosmetics, and in some antibacterial toothpastes
PCBs and dioxins	Incineration processes; paper production; electrical transformers
Phthalates	Plastics
Phytoestrogens	Natural hormones in many plants
Prescription hormones	Estrogen therapy
Pesticides:	
Amitraz, Carbofuran, Chlorpyrifos, DDT, Deltamethrin, Dimethoate, Trichlorfon, Lindane	Insecticides
Vinclozolin, Carbendazim, Benomyl, Penconazole, Prochloraz, Propinconazole, Tridemorph, Epoxyconazole	Fungicides
Atrazine, Linuron, Metiram	Herbicides

Source: Adapted from Reynolds, K. S., Endocrine Disrupts: A New Category of Waterborne Risk. Available at <http://www.wcp.net/archive/apr00ontap.htm>.

food and water. Evaluation of human health impacts of endocrine disruptors has been difficult to document because offspring of exposed individuals usually elicit the effects, which include thyroid dysfunction, lower sperm counts, undescended testicles, and early puberty. Some researchers suggest more efforts should be placed on studying the potential of endocrine disruptors to cause human and environmental harm because of the uncertainties surrounding these chemicals.

The importance of identifying emerging risks associated with substances such as PPCPs and endocrine disruptors is to address potential environmental issues and concerns before they become critical human health and ecological problems. Although conventional *priority pollutants* have received significant attention over the past 30 years, PPCPs and endocrine disruptors have been identified as potential human and environmental issues only in the past 5 to 10 years. With the rapid development of new types and amounts of these substances, we will be adding significantly to the already large array and concentrations of poorly understood PPCP and endocrine disruptor chemicals entering our environment. The *EPA's 2003 Strategic Plan* specifically states that it "will focus on improving our scientific understanding of exposure to, effects from, and management of endocrine-disruptor chemicals and advancing our screening and testing program. We will also conduct research to determine the extent of the impact that endocrine-disrupting chemicals have on humans, wildlife, and the environment."

10.3 ADVERSE EFFECTS

Ecosystem and human/animal exposure and processes involving organic chemicals occur via many pathways and reactions, as noted in Chapter 1 and Table 10.5. The potential for negative environmental impacts and human/animal health effects due to misuse or accidents involving organic chemicals is a concern because of the direct and indirect consequences to surrounding ecosystems and various organisms in addition to the inefficiencies in various cleanup procedures. Care must be taken in the manufacturing, storage, transportation, and handling of organic chemicals. With adequate training and precautions, many incidences of contamination could be avoided.

Several noteworthy examples of *adverse effects* due to pesticide misuse have been detailed in the scientific literature and the popular press. Many studies have cited residual levels of pesticides in soils and aquatic systems as the reason for pesticide toxicity to plants and fish. Bioaccumulation is also of concern because, over time, the absorption or ingestion of low levels of pesticides may accumulate to toxic levels in organisms, then in offspring, or in organisms higher on the food chain.

Table 10.5 Specific Organic Chemical Reactions Involving Different Ecosystems and Organisms

Reaction	Atmosphere	Hydrosphere	Humans and		Animals
			Soils	Vegetation	
Solubility	X	X	X	X	X
Hydrolysis	X	X	X	X	X
Sorption	X	X	X	X	X
Biodegradation	X	X	X	X	X
Photolysis	X	X	X	X	
Volatilization	X	X	X		
Accumulation			X		
Metabolism				X	X
Bioaccumulation				X	X
Respiration				X	X
Excretion					X

Source: Adapted from Ney (1995).

Many of the pesticides are toxic to organisms other than those specifically targeted. At high enough levels, most pesticides can also be toxic to humans. One of the greatest concerns with the development and use of these substances is their slow breakdown and their ability to accumulate in organisms.

However, it should be stated clearly that pesticides, if used properly, can increase food production and control insects (e.g., mosquitoes) that can have a devastating effect on the quality of animal and human life. Currently, *West Nile virus transmission* through mosquitoes has increased public officials' warnings and their advocacy of using N,N-diethyl-m-toluamide (DEET) containing lotions and sprays. Previously these same officials discouraged use of these products because of the potential harm they may cause when absorbed through the dermal (e.g., skin) layer. When confronted with the possibility of death as opposed to short-term exposures, the options to prevent the former succeed.

10.3.1 Human Health

Many toxicological responses are related to the effects of organic chemicals. The simple alkane, alkene, and alkyne hydrocarbons are volatile gases that cause asphyxiate disorders, which result from insufficient oxygen intake. Hydrocarbon liquids are known to cause dermatitis that is associated with the dissolution of fatty skin tissues and results in inflammation, drying, and scaly skin. Other problems associated with some of these substances are irritation, headaches, dizziness, and nervous system disorders that cause muscle weakness and sensory impairment of the hands and feet. Of the *BTEX compounds*, benzene is the most toxic because it is readily absorbed by fatty tissue. Benzene can cause damage to blood-forming cells of bone marrow, skin irritation, headaches, fatigue, and more serious problems depending on the concentration and length of exposure. Although cigarette smoke contains benzene, exposure is 10 to 100 times greater for some industrial workers according to the *Occupational Safety and Health Administration* (OSHA) and the EPA. Even some common household products such as glues, cleaning products, detergents, art supplies, and paint strippers can contain benzene.

Example Problem 10.1

Inhalation exposure of benzene at a level of 7 g/m³ can cause acute poisoning in less than 1 h due to central nervous system failure; exposure to 60 g/m³ can result in death within minutes. Chronic benzene poisoning from long-term exposure to low levels of benzene causes lowered blood counts of white cells and platelets, and bone marrow damage. Low-level exposure of benzene is also a major health risk and can cause acute myelogenous leukemia (AML). Because the major exposure pathway of benzene is through inhalation (>95%), infants (<1 year old) are at great risk due to their low bodyweight and exposure from secondhand smoke and urban pollution.

Calculate the risk associated with benzene inhalation by smoking 20 cigarettes a day. Assume each cigarette contains 55 µg benzene, half of which is absorbed in the lung, and that the individual is physically active (e.g., breathes in 20 m³ of air daily).

$$\text{benzene/day} = \frac{55 \text{ } \mu\text{g benzene}}{\text{cigarette}} \times 0.5 \times 20 \text{ cigarettes/day} = 550 \text{ } \mu\text{g benzene/day}$$

so the daily amount of benzene absorbed due to smoking is

$$\text{daily exposure of benzene from cigarettes} = \frac{550 \text{ } \mu\text{g benzene/day}}{20 \text{ m}^3/\text{day}} = 27.5 \text{ } \mu\text{g/m}^3$$

if the benzene “threshold exposure level” for leukemia is 41 µg/m³, the percentage of benzene contributed due to smoking would be

$$\% \text{ of benzene from smoking} = \frac{27.5 \mu\text{g}/\text{m}^3}{41 \mu\text{g}/\text{m}^3} \times 100 = 67\%$$

If this individual smoked more or was less active (reduced inhalation volume), he or she would possibly receive enough benzene from smoking to exceed the risk associated with leukemia! In fact, research has shown that benzene from heavy smoking contributes to 12 to 58% of leukemia deaths (Korte et al., 2000).

Toluene is less toxic than *benzene*, but inhalation exposure to toluene can result in headaches, nausea, dizziness, and at very high exposure leads to comas. Another PAH, *naphthalene*, which is a fused double aromatic ring structure, can cause skin irritation, dermatitis, headaches, vomiting, and in extreme cases of poisoning death due to kidney failure. Some PAHs can be metabolized to products that are thought to be mutagens and are carcinogenic (see Chapter 13).

Methanol (CH_3OH) can be oxidized to products that affect the central nervous system, the optic nerve, and retinal cells. Individuals who mistakenly consume methanol as an alcoholic beverage can suffer permanent impairment or loss of vision, or in the case of acute exposures possibly death due to cardiac depression. *Phenols* are known to damage spleen, pancreas, and kidney organs and cause gastrointestinal disorders, kidney malfunctions, convulsions, and circulatory system failures. TCE and PCE are known to damage liver and kidney organs, the central nervous system, and are possible human carcinogens. In addition to problems associated with PCBs causing cancer in animals and humans, these chemicals are also known to cause a number of serious noncancer health effects such as impacts on the immune, reproductive, nervous, and endocrine systems. PCBs, which are known endocrine disruptors, can affect human thyroid hormone levels that are responsible for normal growth and development. For example, infants in the Netherlands and Japan that were exposed to PCBs had altered thyroid levels. *Methyl isocyanate* ($\text{CH}_3\text{-N=C=O}$), a highly toxic compound to humans from acute (short-term) exposure, is used principally for the production of carbamate pesticides. In 1984, when several tons of methyl isocyanate were accidentally released into the atmosphere in Bhopal, India, there were approximately 3800 deaths and the injury of another 170,000 people. Pulmonary edema caused most of the deaths, with several deaths also resulting from secondary respiratory infections. Survivors exhibited lung and eye damage, as well as reproductive effects such as increased stillbirths and spontaneous abortions. One of the most toxic organic chemicals manufactured is *nerve gas*, an organophosphorus compound that attacks the central nervous system. Because of its lethal nature, and because the liquid forms are readily adsorbed through skin, as little as 0.01 mg/kg, or a single drop, can result in death.

Pesticides are used to benefit humankind by controlling diseases such as malaria and typhus, and insect outbreaks. However, high doses of some pesticides can be harmful to humans. Paraquat, an organonitrogen herbicide, has been widely used for controlling annual and broadleaf weeds in no-till cropping systems, and is known to enter the human body through inhalation, ingestion, or direct contact. *Paraquat* inhibits enzyme activity and impairs lung, kidney, liver, and heart functions and has caused numerous human deaths. One of the first insecticides, DDT, was introduced in the 1940s to control malaria and typhus. Use and manufacture of DDT, however, were banned in the United States and several other countries in the early 1970s because it attacks the central nervous system, causing eye twitching, tremors, memory loss, and personality disorders. Other organohalide insecticides that have been banned in the United States include aldrin, dieldrin, heptachlor, and chlorodane, all of which can cause headaches, nausea, vomiting, and convulsions. *Parathion*, a phosphorothionate with a history of causing human health problems, was responsible for the deaths of 17 of 79 Jamaicans who were exposed to contaminated flour in 1976. Symptoms of parathion poisoning include skin twitching, breathing problems, and ultimately respiratory failure from paralysis of the central nervous system. Infant and adult deaths have resulted from parathion doses of 2 and 120 mg, respectively. Two *chlorophenoxy herbicides*, 2,4-di- and 2,4,5-trichlorophenoxy acetic acids, better known as 2,4-D and 2,4,5-T, respectively, have also been shown to cause human health problems. High concentrations of 2,4-D can cause nerve impairment, convulsions, and brain damage. Results of a study of

Kansas farmers who worked with 2,4-D suggested they were six to eight times more likely to suffer from non-Hodgkin's lymphoma than nonexposed individuals. A mixture of 2,4-D and 2,4,5-T, also known as *Agent Orange*, was widely used as a defoliant in the Vietnam War. The mixture contained the by-product *tetrachlorodioxin* (TCDD), which is generally called *dioxin*. Dioxin may be highly toxic and cause a skin disorder called chloracne, possible liver and tissue damage, and is a potential carcinogen. Use of 2,4-D and 2,4,5-T has caused human health problems when improperly and indiscriminately introduced into the environment. Although the exposure of humans to high levels of pesticides is relatively low (except in cases of misuse or accidents), we must continue to be aware of the potential impacts of pesticides (Den Hond et al., 2003). Therefore, it is necessary for all those working with pesticides to follow directions and take every precaution to protect themselves, other humans, and our environment from becoming exposed and/or contaminated.

10.3.2 Animals and Wildlife

Laboratory research has shown that high doses of certain pesticides given to animals can cause *cancer, mutagenesis, neuropathy, and death*. Even small doses of some pesticides may result in minor impacts such as skin irritation and breathing problems. PCBs have been demonstrated to cause a variety of adverse animal health effects as mentioned earlier. Animal thyroid hormone levels are known to be affected by PCBs as noted in decreasing rodent thyroid hormone levels that caused both developmental and hearing impairments. The different health effects of PCBs may be interrelated, as alterations in one system may have significant implications for the other systems of the body. Pesticide concentrations given in many *dose-response experiments* with animals are generally well above levels that are recommended by the manufacturers for the intended purpose of the pesticide.

While there is only a causal link between endocrine disruptors exposure and effect in humans, concern exists as evidence surfaces of adverse reproductive and developmental effects in wildlife, which suggests endocrine system impacts. For example, several cases involving animal and wildlife have shown they were adversely affected by endocrine disruptors. These effects have been manifested as abnormal reproduction, thyroid dysfunction, and masculinization or feminization of females and males, respectively. In addition, the birth of birds with crossed beaks, alligators with small penises, and frogs with multiple legs has been attributed to exposure to endocrine disruptors. Research has found an adverse relationship between endocrine disruptors and mating and parenting behavior, sexual development, and breeding of bald eagles, terns, gulls, turtles, harbor seals, beluga whales, as well as other species.

10.3.3 Aquatic Organisms

As noted earlier, low levels of PPCP substances have been detected in various environmental samples. Because pharmaceuticals are designed to cause physiologic effects, the long-term effects of these substances are unknown. Thus, it may be reasonable to conclude that there are impacts on aquatic and terrestrial organisms due to endocrine-disrupting pharmaceuticals released into the environment. Pharmaceuticals and their metabolites are widely distributed, can be persistent, are known to bioaccumulate, and also can mimic other pollutants such as *organochlorine substances*. Low levels of anticholesterol, nonsteroidal anti-inflammatory, and hormone estrone drugs have been detected in numerous water samples, which creates problems in controlling the effects of these potential endocrine disruptors on aquatic species. Impacts of these substances have been suggested by abnormal breeding abilities of lake trout, and overabundance of either male or female populations of different fish species. *Wastewater effluents* displaying estrogenic activity have been shown to affect sexual differentiation in fish, presumably because of an additive response between the natural and synthetic hormones with the same mode of action.

A 1999 study of wastewaters, surface waters, groundwaters, and drinking waters identified antimicrobials, steroids, and more than 50 individual PPCPs (from more than ten broad classes of therapeutic agents and personal care products). Concentrations ranged from nondetectable to sub-ppb

(ng/L) to hundreds of ppb ($\mu\text{g/L}$) (Ternes et al., 2002). Although these levels are very low, continual introduction of these substances into aquatic environments can cause PPCPs to persist due to degradation compensated for by additions or from the recalcitrant nature of specific PPCPs. Much concern has surrounded the identification of hormone disruption in fish by natural and pharmaceutical estrogens, mis- and overuse of antibiotics that leads to resistant pathogens, and the fact that there are many PPCPs currently used. Concerns expressed about fugitive PPCPs include the introduction of pathogen resistance to antibiotics in discharges, influence of natural and *synthetic sex steroids* on aquatic organism endocrine systems, and the unknown consequences of numerous types of PPCPs.

10.3.4 Groundwaters

Organic chemicals are present in surface waters and groundwaters. Groundwater, once thought to be pristine, has been found to contain a broad spectrum of organic chemicals that are both indigenous (natural materials) and anthropogenic (derived from human activities). A study of groundwater commissioned by the U.S. Congress identified approximately 175 different natural and anthropogenic organic chemicals. Another study that examined drinking waters found 14 million Americans were consuming waters that contained traces of pesticides, with those most affected living in the Midwest. Many of the natural organic chemicals, as well as microorganisms present in surface waters and groundwaters, will react with Cl_2 , which is commonly used in drinking water treatment, to produce *trihalomethanes*, a group of volatile halogenated organic compounds. In an EPA survey of pesticides in various groundwater samples in the United States, 67 different pesticides were found in 33 states (a total of 35 states participated in the survey). A total of 17 pesticides in 17 states were detected at levels greater than the *EPA Health Advisory* (HA) level. The percentage of groundwaters exceeding the HA level for any particular pesticide ranged from 0 to 10%. The Office of Technology Assessment also identified 33 principal sources that have the potential for groundwater contamination, and grouped them into six categories.

Table 10.6 Short List of Organic Chemical Sources That Have the Potential to Contaminate Surface Waters, Groundwaters, and Soils

Category	Description	Sources
I	Intentional discharge	Septic tanks and cesspools Injection wells (hazardous wastes) Land application (sludge, wastewater hazardous wastes)
II	Containment	Landfills and open dumps Surface impoundments Waste tailings and piles Animal burial sites Underground storage tanks Storage containers
III	Transportation	Pipelines Rail and truck
IV	Discharge from planned activities	Pesticide application Animal feed operations Urban runoff Atmospheric pollutants
V	Induced flow	Production wells (oil and gas) Construction excavation
VI	Natural	Groundwater–surface water interactions Wetlands Underground deposits (coal, oil, gas)

Source: Office of Technology Assessment (1984).

Table 10.6 lists the six categories of contaminant sources grouped according to the general nature of the source of the organic contaminant.

Undegraded PPCP substances discharged into surface waters can find their way into groundwaters through leaching or recharge processes. Certain pharmaceutically active compounds (e.g., caffeine, aspirin, nicotine) are known to persist in the environment for longer than 20 years. Continued input of these compounds to the aquatic environment may result in groundwater contamination by environmentally persistent PPCP substances.

10.3.5 Plants

Plants can be exposed to various organic pollutants through atmospheric deposition, contaminant spills, irrigation waters, and land-applied materials such as municipal biosolids and animal manures. The mode of action of herbicides refers to the mechanism by which the pesticide kills or interacts with the target plants. Based on their modes of biological action, herbicides are generally classified as either contact or systemic. *Contact herbicides* kill target plants by weakening or disrupting cellular membranes, which, in turn, results in the loss of cellular constituents. If the contact herbicide has an acute reaction with the target plant, death may be extremely rapid. *Systemic herbicides* are designed and manufactured to target certain types of plants specifically, e.g., grasses vs. broadleaves, so that selective control can be maintained. Systemic pesticides must be absorbed or ingested by the target organism so that it may interfere with the organism's physiological (e.g., cell division, chlorophyll formation, tissue development) or metabolic (e.g., respiration, enzyme activity, photosynthesis) processes. Systemic pesticides are generally slow acting and may require days, weeks, or even longer periods before results become evident.

Plants that are sensitive to pesticides can show rapid signs of growth irregularity, loss in biomass, or death. Plants are capable of building up a resistance to certain pesticides if the pesticides are used frequently and at dosages that plants can tolerate. Higher concentrations of the pesticide would

Table 10.7 Effects of Some Herbicides and Insecticides on Nontargeted Plants in Soil and Water Environments

Pesticide Type	Location	Effect
Herbicides		
Aromatic acid	Soil	Carryover in residue affects subsequent crop; soluble herbicides (e.g., picloram) can injure adjacent plants
	Water	Kills or inhibits some aquatic plants
Amides, anilines, nitriles, esters, carbamates	Soil	Some persistence resulting in residue carryover affecting subsequent crop
	Water	Surface erosion may transport herbicide to water bodies
Insecticides		
Organochlorine	Soil	Residue carryover can affect subsequent crops; transport to surface waters may affect aquatic plants
	Water	Contaminated waters can affect plants if waters used for irrigation
Organophosphates, carbonates, pyrethroid	Soil	Usually short-lived, thus little effect to plants
	Water	Toxic to certain algae

Source: Madhun, Y. A. and Freed, V. H., in *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*, H. H. Cheng, Ed., SSSA Book Series No. 2, Soil Science Society of America, Madison, WI, 429–466, 1990. With permission.

then be required to achieve a similar level of control. Pesticides other than herbicides, such as insecticides, can also affect plants that are not the specific target organism the pesticide was designed to control. Table 10.7 lists effects that certain herbicides and insecticides can have on nontargeted plants and microorganisms in soil and water environments.

10.3.6 Microorganisms

Organic chemicals introduced into the environment can have a devastating effect on certain organisms, which may or may not be the intended purpose of the organic chemical. Soil and aquatic ecosystems contain a multitude of microorganisms, many of which are beneficial (see Chapter 3). Contamination of these ecosystems by organic chemicals, such as when high concentrations of pesticides are inadvertently used or when surface runoff containing pesticides is introduced into surface waters, can reduce microbial activity. However, in some situations enhancement of microbial activity may occur.

The theoretical response of soil microorganisms to different herbicides, shown in Figure 10.2, could also be related to organic chemicals other than herbicides and to plant responses over time

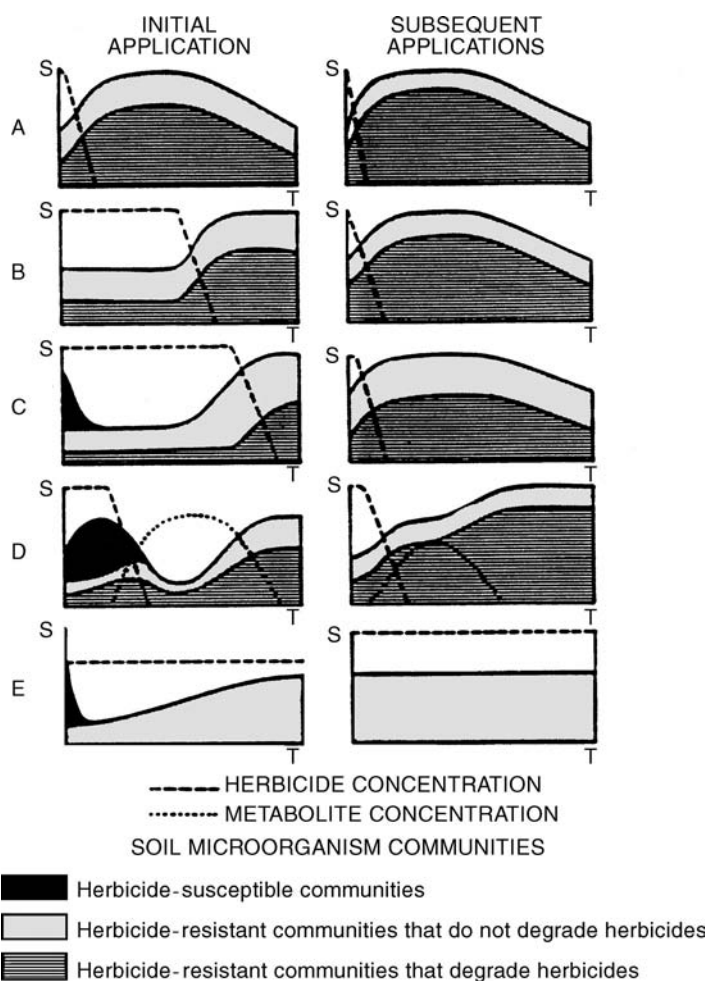


Figure 10.2 Theoretical response of soil microbial communities and degradation rates of herbicides (A through E) over time. Illustrations represent initial (left side) and subsequent (right side) applications. Time is represented on the abscissa and herbicide concentration on the ordinate axis. (Redrawn from Cullimore, 1971.)

to various pesticides. “Initial application” in Figure 10.2 represents the first time the herbicide was used. “Subsequent applications” refers to the response of the ecological system to continued application of the herbicide. The initial herbicide effect can be summarized as follows: herbicide A = no inhibition of soil microorganisms, rapid degradation rate, increase in microbial populations; herbicide B = no inhibition of soil microorganisms, moderate degradation rate, increase in microbial populations; herbicide C = kills sensitive soil microorganisms, increase in herbicide-degrading microorganisms over time, slow degradation rate; herbicide D = initially herbicide kills sensitive microorganisms, herbicide metabolites build up and inhibit certain microorganisms, resistant microorganisms eventually degrade herbicide; herbicide E = kills sensitive microorganisms, resistant microorganisms increase but do not degrade herbicide. Upon further herbicide application, herbicides A, B, and C are rapidly degraded; herbicide D and its metabolites are degraded at a faster rate; and herbicide E concentrations build up due to lack of degrading microorganisms. These are just a few examples of how soil ecosystems and plants might respond to organic chemical inputs. In an extreme case of contamination, the number and activity of soil microorganisms may be reduced to essentially zero.

10.4 PREDICTING THE FATE OF ORGANIC CHEMICALS IN THE ENVIRONMENT

Reliable predictions of the movement and fate of organic chemicals (Figure 10.3) are important for determining the impact of organic chemicals on our environment. Proper

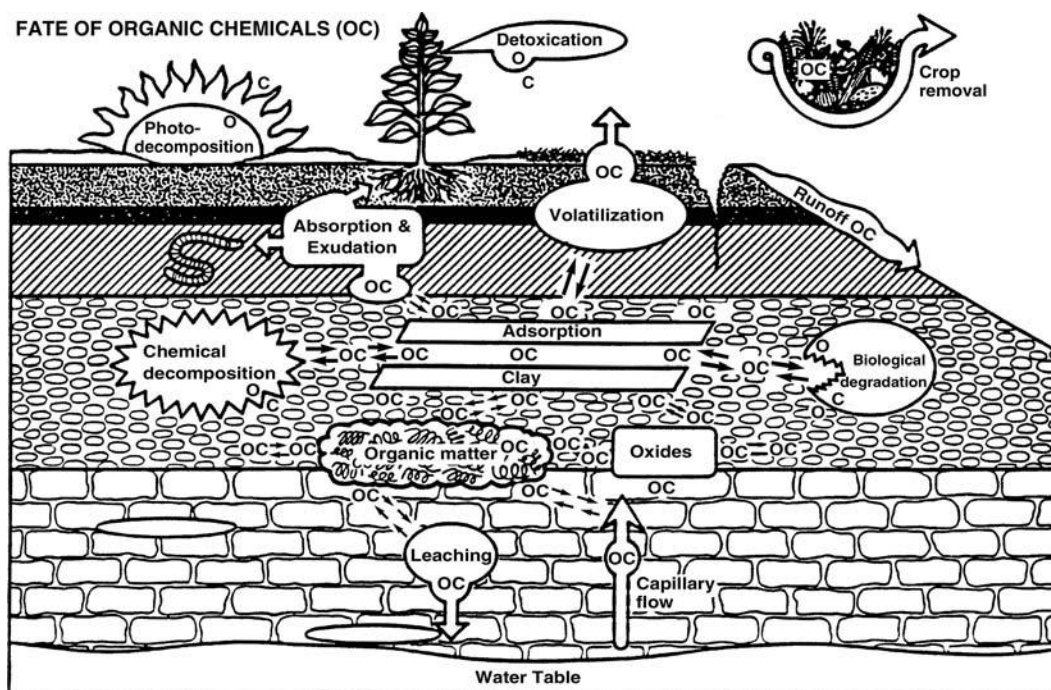


Figure 10.3 Processes and fate of organic chemicals (OCs) in the environment. Both transfer and degradation processes are depicted in the figure; in transfer processes the OC is intact, whereas in degradation processes the OC is separated (O/C). (Adapted from Weber, J. B. and Miller, C. T., in *Reactions and Movement of Organic Chemicals in Soils*, Soil Science Society of America, Madison, WI, 305–334, 1989.)

disposal of wastes and use of pesticides (as well as all chemicals) require knowledge of factors that can influence their mobility and transformation, as well as human safety, environmental quality, and pesticide efficacy. Surrounding ecosystems can be affected if conditions are conducive to organic chemical drift, leaching, or surface runoff. Table 10.8 outlines some of the factors related to pesticide use that can affect environmental quality and pesticide effectiveness.

The mobility of organic chemicals and their ultimate degradation after being introduced into the soil environment are determined by chemical, physical, and biological processes. Each organic chemical has its own molecular structure that determines, at least partially, the degree to which it will react in soils. Some organic chemicals contain charged functional groups (see Table 10.2) that enhance the chance of the chemical being adsorbed to soils; positively charged organic chemicals are adsorbed to the negatively charged sites on soil clays and organic matter (see Chapter 3 for more information on soil properties). Other organic chemicals may persist (e.g., recalcitrant organic compounds) in soils for long periods of time if chemical and microbial transformations are suppressed due to the toxicity of the organic chemical.

The *transfer and degradation processes* controlling the movement and fate of organic chemicals are listed in Table 10.9. Physical drift is generally a concern during the application of pesticides, but could also occur at times of high winds or during rainstorms when pesticides are washed off vegetation. Small droplets have a greater potential for being transported by wind action than do large droplets. Other processes are generally related to what happens to the organic chemicals in the soil environment. In the next sections, we discuss many of these processes and other characteristics of organic chemicals that influence their fate and transport.

Table 10.8 Impacts of Pesticide Management Decisions on Both Environmental Quality and Pest Control Efficacy

Management Decision	Impacts	
	Environmental Quality	Pest Control
Type of pesticide	High sorption — low leaching Fast degradation — not transported Toxicity — determines maximum allowable concentration in water	Efficacy of control dependent on pesticide
Type of application	Soil incorporated — greater chance for groundwater contamination Ground application — decreases risk of pesticide drift	Toxicity to target pest enhanced by proximity of pesticide to target Wet soil conditions may hinder optimum time of application
Spray technology	Large droplets — reduced physical drift	Large drops may decrease efficacy
Timing of application	Close to rainfall or irrigation — increases chance for groundwater contamination	Efficacy of pesticide depends on proper timing
Irrigation schedule	Planned irrigation — reduces potential for groundwater or surface water contamination	Changes in soil moisture may affect pests
Tillage practice	Minimum tillage effects — reduces runoff, requires increased levels of pesticide, greater risk of pesticide leaching and drift	Increases pest densities that require additional need for pesticides
Proper application procedures	Pesticide spills or misuse — increases water and soil contamination	No negative effect on pest control

Source: Shoemaker (1989).

Table 10.9 Movement and Fate of Organic Chemicals in the Environment, with Particular Reference to Pesticides

Process	Consequence	Factors
Transfer (<i>processes that relocate organic chemicals without altering their structure</i>)		
Physical drift	Movement of organic chemical due to wind action	Wind speed, size of droplet, distance to physical object
Volatilization	Loss of organic chemical due to evaporation from soil, plant, or aquatic ecosystems	Vapor pressure, wind speed, temperature
Adsorption	Removal of organic chemical by interacting with plants, soils, and sediments	Clay and organic matter content, clay type, moisture
Absorption	Uptake of organic chemical by plant roots or animal ingestion	Cell membrane transport, contact time, and susceptibility
Leaching	Translocation of organic chemical either laterally or downward through soils	Water content, macropores, soil texture, clay and organic matter content, rainfall intensity, irrigation
Erosion	Movement of organic chemical by water or wind action	Rainfall, wind speed, size of clay and organic matter particles with adsorbed organic chemicals on them
Degradation (<i>processes that alter the organic chemical structure</i>)		
Photochemical	Breakdown of organic chemicals due to the absorption of sunlight (i.e., UV light)	Structure of organic chemical, intensity and duration of sunlight, exposure
Microbial	Degradation of organic chemicals by microorganisms (see Chapter 3 for discussion on soil microorganisms)	Environmental factors (pH, moisture, temperature) nutrient status, organic matter content
Chemical	Alteration of organic chemical by chemical processes such as hydrolysis, and redox reactions	High and low pH, same factors as for microbial degradation
Metabolism	Chemical transformation of organic chemical after being absorbed by plants or animals	Ability to be absorbed, organism metabolism, interactions within the organism

Source: Marathon-Agricultural and Environmental Consulting Inc., Video Cassettes — Fate of Pesticides in the Environment, 1992.

10.4.1 Plant Uptake

Organic chemicals, such as herbicides, are absorbed by plants either through their roots or aboveground foliage. *Uptake* is dependent on the organic chemical and the plant species. Seeds are also capable of adsorbing organic chemicals either before or after seed germination. Adsorption of organic chemicals on the outer surface of seeds increases the chance of absorption, which can take place by nonmetabolic processes when seeds imbibe water or through diffusion processes. Factors that influence seed uptake of organic chemicals are related to the properties of the chemical (concentration, structure, solubility, and diffusion rate), soil (temperature and pH), and seed (size, characteristics and permeability of the seed coat).

Plants are also capable of absorbing organic chemicals through their aboveground parts, including stems, buds, and leaves. Succulent and perennial woody plants are noted for the uptake of herbicides through their stems. Buds are the primary targets of contact herbicides because entry generally guarantees plant kill. Leaves absorb organic chemicals from both the upper and lower leaf surfaces; however, absorption is often faster through the lower surface because it has a thinner

cuticle. *Nonpolar organic chemicals* enter into leaves more readily than do *polar organic chemicals*, or many inorganic constituents. The mechanism of entry for oily and aqueous solutions is believed to follow different pathways.

Most organic chemicals can be readily taken up by roots and foliage and transported through plants by two systems — the *symplast* (living plant tissue) and *apoplast* (nonliving plant tissue). Organic chemicals that enter the symplasts are exposed to enzymes capable of altering foreign substances. However, the symplast is enclosed by the apoplast, thus preventing direct contact between organic chemicals and the living tissue of the symplasts. The apoplast consists of cell walls and xylem that form an interconnected continuum throughout the plant. It is within the apoplast that toxic pesticides and other organic chemicals can be translocated over short and long distances in plants.

Once absorbed by plants, organic chemicals can be transformed by several reactions that alter the organic chemicals. For example, plants that are capable of absorbing herbicides, and other organic contaminants, may be able to transform or metabolize these organic chemicals to nonphytotoxic levels by one or more of the following reactions: *oxidation–reduction*, *hydrolysis*, *hydroxylation*, *dehalogenation*, *dealkylation*, *conjugation*, or *β -oxidation*. Each of these reactions alters the structure of the organic chemical and thus its chemical nature. Although plants are similar to microorganisms, insects, and mammals in their capability to metabolize organic chemicals, rates of plant transformations are generally slower, which in some cases can result in greater toxicity of the organic chemical to the plant.

10.4.2 Solubility

The *solubility* of an organic chemical is important to its fate and mobility, primarily because highly soluble chemicals tend to be rapidly distributed within soil and water systems. Aqueous solubility of organic chemicals is determined based on the total amount that dissolves in pure water at a specified temperature. When the aqueous solubility of an organic chemical is exceeded, a separate phase will exist in addition to the aqueous solution. All organic chemicals are soluble in water to some degree, although the amount dissolved is highly variable among the different organic compounds. Because water is a polar compound, and similar types of compounds tend to interact, it is not surprising that polar organic chemicals are generally more water soluble than nonpolar substances. Solubilities of common organic chemicals generally fall in the range of 1 to 100,000 mg/kg (weight of organic chemical per weight of pure water); however, many have higher solubilities. The difference between the least soluble and most soluble organic chemicals is approximately 1 billion-fold (see Figure 10.4 for the range in solubilities for specific groups of organic chemicals).

Solubility of organic chemicals in water is a function of temperature, pH, ionic strength (concentration of soluble salts), and the presence of other organic chemicals such as dissolved organic carbon (DOC). Most organic chemicals become more soluble with increasing temperature. The solubility of organic acids generally increases with increasing pH, whereas organic bases are expected to behave in an opposite manner. Soluble salts will commonly reduce organic chemical solubility, which explains why organic chemicals tend to be less soluble in oceans than in freshwaters. Several studies have indicated there is usually an increase in the solubility of many low-water-soluble organic chemicals with higher levels of DOC.

Various methods are used to estimate organic chemical solubilities. In addition to direct solubility measurements, two frequently used methods are based on (1) chemical structure and (2) octanol–water partition coefficients. The former method was developed to estimate the aqueous solubility of particular groups of compounds, for example, aliphatic and aromatic hydrocarbons. A significant amount of data is available on the relationship between aqueous solubility and *octanol–water partition coefficients* (K_{ow} values). The K_{ow} for a specific organic compound is determined by allowing the

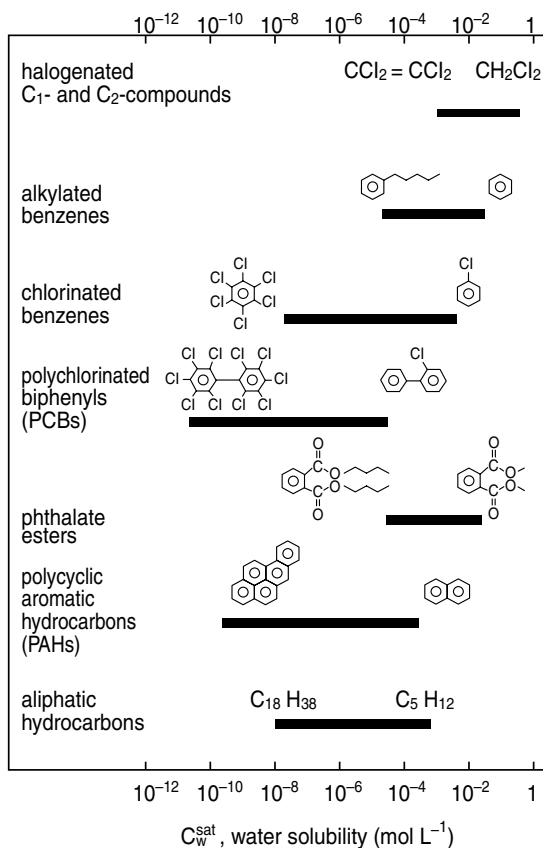


Figure 10.4 Variation in the range of water solubilities for specific classes of important organic chemicals. (Adapted from Schwarzenbach, R. P. et al., *Environmental Organic Chemistry*, John Wiley & Sons, New York, 1993. With permission.)

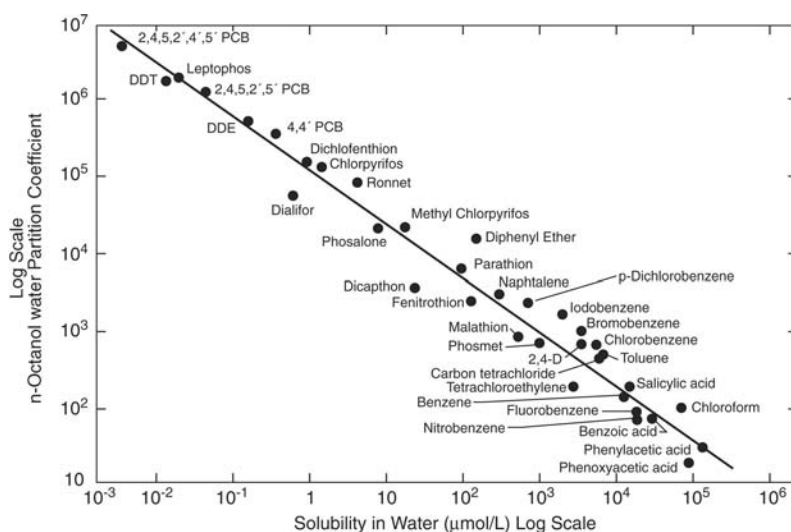


Figure 10.5 Relationship between octanol-water partition coefficients (K_{ow}) and solubility of several organic chemicals. Note the extensive range in solubilities of the organic chemicals. (From Chiou, C. T. et al., *Environ. Sci. Technol.*, 11, 475, 1977. With permission.)

compound to partition into two immiscible phases (octanol and water) that are in contact with each other. At equilibrium, the concentration of the compound in the octanol and/or that in the water are determined for calculation of K_{ow} using the following equation:

$$K_{ow} = \frac{\text{amount of organic chemical in octanol (mg/L)}}{\text{amount of organic chemical in water (mg/L)}} \quad (10.1)$$

The relationship between water solubility and K_{ow} is shown in Figure 10.5. As shown in this figure, there is an inverse and log-log linear relationship between solubility and K_{ow} .

Example Problem 10.2

The solubility of an organic chemical is ten times greater in octanol than in water. Calculate the amount extracted from a 100-mL river water sample that contains 5 mg of the organic chemical using a 50 mL volume of octanol. First, consider the relationship defined in Equation 10.1.

$$K_{OW} = \frac{\text{amount in octanol (mg/L)}}{\text{amount in water (mg/L)}} = \frac{x \text{ mg}/50 \text{ ml}}{(5 - x) \text{ mg}/100 \text{ ml}}$$

using a K_{ow} of 10, the equation can be rearranged to

$$10 = \frac{x \text{ mg}/50 \text{ ml}}{(5 - x) \text{ mg}/100 \text{ ml}} \text{ and } 10(5 - x) \text{ mg} = \frac{100 \text{ ml } x \text{ mg}}{50 \text{ ml}} = 2x \text{ mg}$$

therefore,

$$(50 - 10x) \text{ mg} = 2x \text{ mg} \quad \text{or} \quad 50 \text{ mg} = 2x \text{ mg} + 10x \text{ mg} = 12x \text{ mg}$$

so,

$$x = 50/12 \text{ mg} = 4.17 \text{ mg}$$

and

$$4.17/5 \text{ mg} \times 100 = 83\% \text{ partitioned into octanol}$$

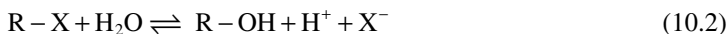
10.4.3 Half-Life

The *half-life* ($t_{1/2}$) of a reaction refers to the amount of time required for half of the reactant to be converted into product or when the reactant concentration is half of its initial level. For organic chemicals, $t_{1/2}$ can be calculated for different types of reactions such as *volatilization*, *photolysis* (decomposition by sunlight), *leaching potential* (adsorption–desorption characteristics), and *degradation* (chemical and microbial). Half-life values are important for understanding the potential environmental impact of an organic chemical. For example, if a highly toxic organic contaminant is accidentally spilled into a lake and the rate of photolysis is rapid (suggesting a small $t_{1/2}$), the consequences may be minimal if the photolysis products are harmless. However, if a moderately toxic contaminant is spilled, and it has a very slow rate of photolysis (indicating a large $t_{1/2}$), then the environmental impacts may be substantial. This kind of scenario can also be used to determine

environmental impacts related to volatilization, leaching potential, degradation characteristics, and other processes that affect organic chemicals in the environment.

10.4.4 Hydrolysis

Hydrolysis reactions occur in soil and aqueous environments due to the action of water. Hydrolysis involves the chemical reaction between an organic chemical and water that results in the breaking of one bond while forming a new C–O bond, i.e.,



where R–X represents an organic chemical and X is a reactive functional group involved in the hydrolysis reaction. Hydrolysis is considered an important reaction that determines the fate of organic chemicals in soil and aquatic environments. Not all organic chemicals can undergo hydrolysis because many of these compounds do not possess functional groups susceptible to hydrolysis (Table 10.10). Hydrolysis reactions are also generally pH dependent.

Half-lives of hydrolysis reactions that follow *first-order kinetics* at a constant pH can be described by the equation:

$$t_{1/2} = 0.693/k_h \quad (10.3)$$

where k_h is the *hydrolysis rate constant* for the first-order kinetic reaction:

$$\partial C / \partial T = -k_h C \quad (10.4)$$

Table 10.10 Examples of Organic Compounds and Functional Groups That Are Either Resistant or Potentially Susceptible to Hydrolysis

Resistant	Susceptible
Alkanes, alkenes, alkynes	Alkyl halides
Benzene/biphenyls	Amides
PAHs	Amines
Halogenated aromatics/PCBs	Carbamates
Dieldrin/aldrin and related	Carboxylic acid esters
halogenated hydrocarbon pesticides	Epoxides
Aromatic amines	Nitriles
Alcohols	Phosphonic acid esters
Phenols	Phosphoric acid esters
Glycol	Sulfonic acid esters
Ethers	Sulfuric acid esters
Aldehydes	
Ketones	
Carboxylic acids	

Source: Harris, J. C., in *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*, W. J. Lyman et al., Eds., McGraw-Hill, New York, chap. 7, 1982a.

three $t_{1/2}$,

$$C_f = 0.25C_i/2 = 0.125C_i = 12.5\%C_i$$

or

number (x) of $t_{1/2}$

$$C_f = (1/2)^x C_i = (1/2)^x 100(\%)C_i$$

where C_f and C_i are final and initial concentrations, respectively.

10.4.5 Volatilization

Volatilization of natural and synthetic organic chemicals in water is responsible for the transfer of these compounds from aquatic and soil environments into the atmosphere. In comparison with volatilization, the process of *evaporation* is related to organic substances that vaporize from an organic phase (e.g., gasoline spill) to the atmosphere. In some cases, volatilization is responsible

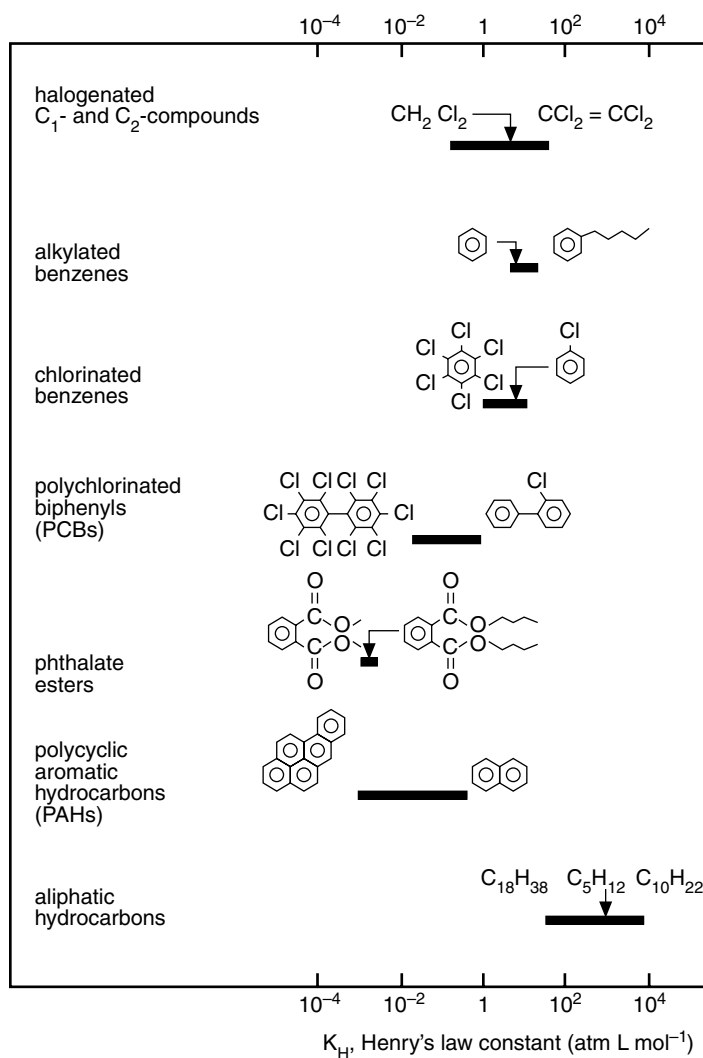


Figure 10.7 Variation in Henry's law constants for several classes of important organic chemicals. (From Schwarzenbach R. P. et al., *Environmental Organic Chemistry*, John Wiley & Sons, New York, 1993. With permission.)

for the gaseous movement of certain organic chemicals that have leached or been introduced into subsurface environments, i.e., the vadose zone. Information on the rate at which organic chemicals volatilize is important for understanding their persistence in soil and aqueous environments. For example, surface waters or soils contaminated by volatile organic chemicals may possibly be cleaned up by either evaporation or volatilization processes (see Chapter 12 for more information on remediation).

The volatilization of contaminants from waters depends on the chemical and physical properties of the organic chemical (solubility and vapor pressure), interactions with suspended materials and sediment, physical properties of the water body (depth, velocity, and turbulence), and properties of the water–atmosphere interface. The solubility of a gas in water is defined by its *Henry's law constant*, which is related to the partial pressure of the gas in a gas–liquid mixture, and is defined as

$$K_H = P_{\text{gas}}/C_{\text{aq}} \quad (10.5)$$

in which K_H is the Henry's law constant, P_{gas} is the partial pressure of the gas, and C_{aq} is the aqueous concentration of the gas. The K_H values for several classes of organic chemicals are shown in Figure 10.7. Large K_H values suggest the organic chemical has a strong tendency to escape from the water phase into the atmosphere. Rates of volatilization, expressed as half-lives, are also important and can vary from hours to years or more. Half-lives for the volatilization of TCE and the pesticide dieldrin from water have been estimated at 3 to 5 h for TCE and close to a year for dieldrin. Table 10.11 lists some additional organic chemicals and their potential for volatilization from water.

Factors that influence the volatility of organic chemicals from soils include intrinsic physio-chemical properties of the chemical (vapor pressure, solubility, structure and nature of functional

Table 10.11 Examples of Organic Chemicals and Their Potential Volatility from Water

Volatility Potential	Organic Chemical	Half-Life ($t_{1/2}$)
Low	Dieldrin	327 d
	3-Bromo-1-propanol	390 d
Medium	Penanthrene	31 h
	Pentachlorophenol	17 d
	DDT	45 h
	Aldrin	68 h
	Lindane	115 d
High	Benzene	2.7 h
	Toluene	2.9 h
	o-Xylene	3.2 h
	Carbon tetrachloride	3.7 h
	Biphenyl	4.3 h
	Trichloroethylene	3.4 h

Note: Half-lives given in days (d) or hours (h).

Source: Thomas, R. G., in *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*, W. J. Lyman et al., Eds., McGraw-Hill, New York, 1982. With permission.

groups, and sorption–desorption characteristics), concentration, soil properties (soil moisture content, porosity, density, organic matter and clay contents), and environmental factors (temperature, humidity, and wind speed). The initial step in the volatilization of some organic chemicals from soils is the ability to change from a solid or liquid in the soil solution to a vapor. After this, the vapor moves through the soil and disperses into the atmosphere by diffusion or turbulence. Laboratory and field measurements of volatilization half-lives for several pesticides range from 1.0 to 1.5 days for trifluralin to 42 to 45 days for DDT and atrazine, respectively.

10.4.6 Photolysis

Photochemical reactions involving sunlight are extremely important in determining the fate of contaminants in aquatic environments, and may also play a role in the degradation of organic chemicals at soil surfaces. In aquatic environments, photolysis can occur by direct or indirect processes. For *direct photolysis*, sunlight is absorbed directly by the organic chemical resulting in a chemical transformation. The rate of direct photolysis is dependent on sunlight intensity and overlapping spectral characteristics of solar radiation and the organic chemical. With *indirect photolysis*, other substances such as DOC, clay minerals, or inorganic elemental species absorb sunlight energy and either initiate a series of reactions that ultimately transform the organic chemical or transfer the excitation energy to the organic chemical.

Atmospheric ozone absorbs solar radiation at wavelengths below 290 nm. Therefore, direct photolysis by sunlight will not occur if the organic chemical in question does not absorb radiation

Table 10.12 Half-Life ($t_{1/2}$) Values for Several Organic Chemicals That Undergo Direct Photolysis

Class	Organic Chemical	Half-Life ($t_{1/2}$)
Pesticides	Trifluralin	~1 h
	Malathion	15 h
	Carbaryl	50 h
	Sevin	11 d
	Methoxychlor	29 d
	2,4-D methyl ester	62 d
	Mirex	1 y
PAHs	Pyrene	0.7 h
	Benz[a]anthracene	3.3 h
	Phenanthrene	8.4 h
	Fluoranthene	21 h
	Naphthalene	70 h
Miscellaneous	Benz[f]quinoline	1 h
	Quinoline	5–21 d
	<i>p</i> -Cresol	35 d

Note: Half-lives given in days (d), hours (h), or years (y).

Source: Harris, J. C., in *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*, W. J. Lyman et al., Eds., McGraw-Hill, New York, 1982b. With permission.

at wavelengths above 290 nm. The intensity of sunlight that reaches the Earth's surface is determined by the thickness of the atmosphere and the angle of incident radiation, which is dependent on latitude, season, and time of day. Sunlight intensity is greatest in summer and least in winter.

Half-lives of organic chemicals that undergo photolysis in aqueous environments are generally in the range of hours to months. Photolysis half-life values for pesticides, PAHs, and some miscellaneous compounds are listed in Table 10.12. Unlike aqueous environments, photolysis reactions in soils are difficult to determine because of the heterogeneous nature of soils and the lack of sunlight penetration. Therefore, photolysis is primarily a surface phenomenon that can be prevented by incorporating the chemical into the soil.

10.4.7 Sorption–Desorption

Sorption–desorption behavior between organic chemicals and soils and sediments is conceivably the most important process affecting organic contaminants (see Chapter 3). Understanding the interactions that occur between soils or aquatic sediments and organic chemicals is important in determining contaminant behavior and, therefore, its movement and fate in the environment. Predictive modeling of contaminant fate and transport requires reliable information on the sorption–desorption behavior of contaminants under variable conditions. Sorption of organic chemicals by clay minerals and soil organic matter occurs by one or more of the following interactions: H-bonding, dipole–dipole interaction, ion-exchange, covalent bonding, protonation, ligand exchange, cation bridging, water bridging, and/or hydrophobic partitioning.

Sorption of many contaminants by soils and sediments has been shown to be an effective means of reducing the mobility of an organic chemical as well as its bioactivity, persistence, biodegradability, leachability, and volatility. The type and nature of functional groups on an organic chemical largely determine its ability to be adsorbed. In soils, clay and metal oxide surfaces and organic matter are the dominant materials responsible for the sorption of organic contaminants. Clay surfaces can act as adsorption sites for one contaminant that in turn can influence the sorption of other contaminants. An example of this is discussed below as a method for the containment of organic contaminants.

For many organic chemicals, and especially nonpolar organic substances, the amount of sorbed compound is directly proportional to the solution concentrations. The distribution coefficient, K_d , for these organic chemicals can be calculated using the partition model (therefore, K_d is sometimes called the *partition coefficient*, K_p , for organics), which is equivalent to the *Freundlich* equation with $1/n$ equal to approximately 1 (see Chapter 3 for further discussion of adsorption processes and modeling):

$$K_d = \frac{x/m}{C_e} = \frac{\text{organic chemical adsorbed per unit weight of soil (mmol/kg)}}{\text{Equilibrium concentration of the organic chemical (mmol/L)}} \quad (10.6)$$

Using K_d and *soil organic C* (SOC), another constant can be determined that is independent of soil type and is specific for the organic compound investigated. The new partitioning constant is related to the organic chemical's sorption characteristics, e.g., its K_d , and the fact that most of the sorption in soils is directly related to the SOC content.

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (10.7)$$

where f_{OC} is the fraction of soil OC, e.g., %OC/100. The K_{OC} is essentially a coefficient that describes the distribution of an organic chemical between the aqueous and soil organic matter phases. As

they are relatively constant, K_{OC} values are often used to predict K_d values for soils with known OC contents. The K_d value, in turn, defines the distribution of the organic chemical between soil solid (sorbent) and solution phases. It is important to note that a K_{OC} value for any given nonpolar organic compound may also be predicted from either the compound's *water solubility* (S_w) or the octanol–water partition coefficient, K_{ow} . In addition, K_{OC} values are inversely and log-log linearly related to S_w , and directly and log-log linearly to K_{ow} . This is a powerful tool, as the environmental fate of a compound (specifically, its retention characteristics) in a soil may be predicted with knowledge of basic characteristics (which are easily obtained), e.g., S_w and the SOC of the soil of interest. Also, K_d values are specific to one point on an *isotherm*, while a partition coefficient, K_p , is the slope of the isotherm, and generally represents the average of the K_d values of each point on the isotherm.

Example Problem 10.4

Sorption of a nonionizable hydrophobic organic chemical by soils with different OC levels was found to be highly variable, as shown by the distribution coefficients (K_d) listed below. However, after normalizing to the OC content the OC-corrected constants, K_{OC} , were approximately the same.

Soil	%OC	K_d	$\log K_{OC}$
1	3.7	35,000	5.98
2	2.8	25,000	5.95
3	8.3	85,000	6.01
4	1.2	10,000	5.92
5	11.8	125,000	6.03

There are two ways of determining an overall K_{OC} value for a particular organic chemical. The first method averages the individual K_{OC} values determined from separate soils, which in the example above would result in a $\log K_{OC}$ of 5.98. A more precise way of calculating K_{OC} values from a number of soils is to determine linear regression statistics for a plot of K_d vs. f_{OC} (e.g., %OC/100) that provide slope and correlation coefficients (r^2) that define the overall K_{OC} and fit of the data, respectively. Note the data should be calculated with the y -intercept as zero. For the data above, $\log K_{OC}$ equals 6.01 with an r^2 of 0.995.

Recent studies have shown that certain organic chemicals, once adsorbed onto soil, clays and claylike materials, can provide an effective sorption barrier to the leaching of other organic contaminants. The organic chemicals used for these studies are often organic cations from a group of organic chemicals called surfactants. Surfactants are compounds that contain a polar or ionic “head” and a nonpolar tail. *Quaternary ammonium cations* (QUATS) are surfactant-like substances containing a protonated amine functional group as the head, $R-NH_3^+$, and an aliphatic carbon tail (Figure 10.8). These compounds are generally inexpensive and widely used in such products as detergents, fabric softeners, antistatic sprays, and swimming pool additives. Modified soils and subsurface materials can be formed *in situ* by injecting QUATS into an area around contaminated sites, to prevent contaminant migration, as the hydrophobic aliphatic tails effectively sorb nonpolar compounds from the soil solution. In addition, organoclays can be prepared and injected as a slurry to form an effective barrier around contaminated sites as well. Because organoclays are capable of sorbing petroleum constituents such as benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylene (BTEX compounds), as well as a variety of other organic contaminants, they should be useful as a liner material around petroleum tank farms, underground

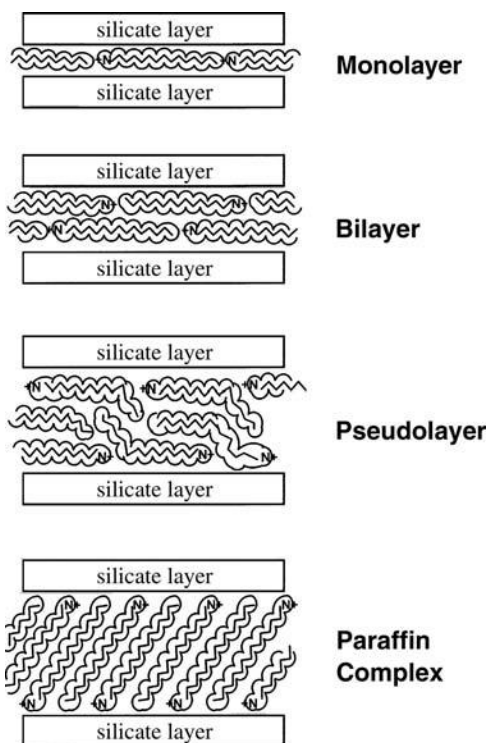


Figure 10.8 Examples of interlayer arrangements of organic cations in swelling 2:1 clays. The organoclays can be used to partition (remove from aqueous solution) nonpolar organic contaminants in water. Organic clays are classified as monolayer, bilayer, pseudolayer, and paraffin complex. (Adapted from Jaynes and Vance, 1996.)

storage tanks, and possibly for treatment of petroleum-contaminated waters. Examples of organoclays are shown in Figure 10.8.

10.4.8 Abiotic and Biotic Transformations

Both abiotic (nonbiological) and biotic (biological) reactions, alone or in combination, are responsible for the transformations of organic chemicals in soil and aquatic environments. Under certain conditions abiotic reactions may dominate, whereas under other conditions biotic reactions may prevail. Degradation of organic chemicals is often assumed to result from biotic processes; however, abiotic reactions may occur simultaneously. Many organic chemical transformations are mediated by microorganisms, but often the actual reaction is an abiotic process.

The principal *abiotic transformation* reactions that occur in aquatic environments include sorption, hydrolysis, oxidation–reduction (redox), and photolysis, whereas in sediments, sorption, hydrolysis, and redox reactions are the dominant abiotic reactions. Oxidation reactions that take place in aquatic environments can be mediated by direct or indirect photolysis reactions, which depend on the organic chemical and substrates present. Nonphotolytic oxidation of organic chemicals can occur directly by reactions involving ozone, or via catalytic pathways with certain metals. *Abiotic reduction* reactions that influence organic chemical transformations may also be catalyzed by certain metal species, with ferrous iron (Fe^{2+}) and the manganous ion (Mn^{2+}) the most important. Redox reactions that occur in sediments follow a similar route as shown for soils (see Chapter 3 for further discussion of redox reactions).

In soils, abiotic transformations take place in the liquid phase (i.e., soil solution) and at the solid–liquid interface. In the soil solution, hydrolysis and redox reactions are the most common abiotic transformations, although a number of other reactions also occur. Clays, organic matter, and metal oxides are capable of catalyzing abiotic reactions that occur in soils. Some exchangeable cations, e.g., copper (Cu) and Mn, can also influence the transformation of organic chemicals. Sorption, hydrolysis, and redox chemical reactions are the dominant abiotic reactions that take place in most soil ecosystems.

Microbial transformations of organic chemicals are classified as: (1) biodegradation (contaminant used as substrate for growth, i.e., metabolism); (2) cometabolism (contaminant is transformed by metabolic reactions without being used as an energy source); (3) accumulation (contaminant is incorporated into the microorganism); (4) polymerization or conjugation (contaminant is bound to another organic chemical); and (5) secondary effects of microbial activity (contaminant is transformed due to indirect microbial effects, i.e., increases or decreases in soil solution pH or modification to the redox status of the soil). Although these transformations are considered mediated by microorganisms, abiotic transformations are also involved, especially in the transformations related to categories 4 and 5.

Biodegradation is considered the primary mechanism by which organic chemicals are transformed to inorganic products such as CO_2 , H_2O , and mineral salts. The metabolism of organic chemicals in soils by bacteria is typically greater than for other microorganisms. In natural ecosystems, biodegradation of organic chemicals is facilitated primarily by heterotrophic bacteria and actinomycetes, certain autotrophic bacteria, fungi (including *Basidiomycetes*) and yeasts, and specific protozoa.

Anaerobic (absence of O_2 , e.g., anoxic) transformation of organic chemicals results in different end products than do aerobic transformations. Because metabolic processes require free oxygen for maximum energy production, in anoxic environments energy recovery is reduced and different organic chemicals result as end products. In a general sense, products resulting from complete mineralization of an organic chemical include primarily CO_2 , H_2O , and salts; but under anoxic conditions, organic chemicals are incompletely metabolized to intermediate substances and end products of *methane* (CH_4), CO_2 , *alcohols*, and organic acids such as *formic* (HCOOH), *acetic* (CH_3COOH), *butyric* ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$), *lactic* ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$), and *succinic* ($\text{HOOCCH}_2\text{CH}_2\text{COOH}$) acids. For example, DDT biodegradation under aerobic and anoxic conditions results in different organic chemicals as shown in Figure 10.9.

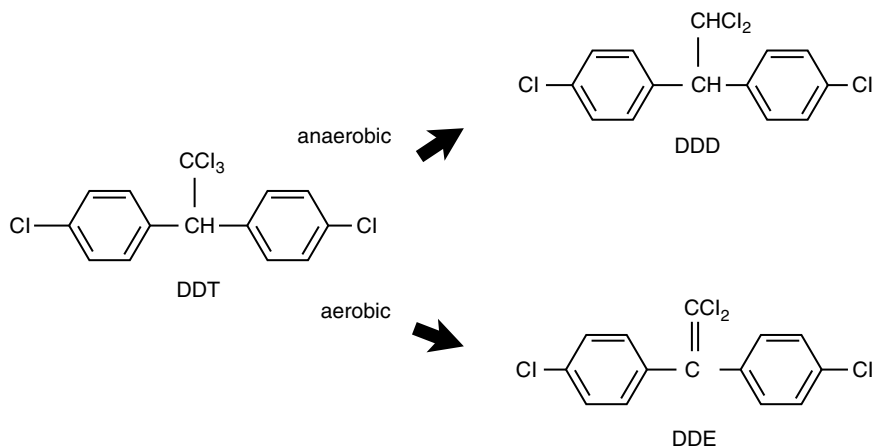


Figure 10.9 Example of anaerobic and aerobic products resulting from biological transformation of the organic chemical DDT.

10.4.9 Response of Organic Chemicals in the Environment

Once introduced into a soil or an aquatic ecosystem, organic chemicals can be translocated, transformed, or persist as a result of the factors described in the previous sections. Processes that result in the translocation of organic chemicals in the soil environment include plant uptake (e.g., absorption), runoff of dissolved or adsorbed species, volatilization and migration in the vapor phase, and leaching as a water-soluble chemical. Clearly, organic chemicals strongly sorbed to organic matter and other soil minerals will not migrate to a large extent unless the particle moves due to erosion or leaches downward as a colloid material. In surface waters, organic chemicals that are volatile may move rapidly into the atmosphere depending on climatic conditions and aquatic system properties. Transformation of organic chemicals by chemical, biological, and photolytic processes may alter their translocation and persistence in soil and surface water environments, which is extremely important for organic chemicals that become more toxic or affect future agricultural practices (e.g., next year's crop) as the modified or transformed substance.

To evaluate organic chemicals in the environment properly, we should have an appreciation of those factors that specifically influence the *translocation*, *transformation*, and *persistence* of these substances. Table 10.13 describes the general range of organic chemical properties that can potentially influence the environmental fate and transport of organic chemicals. Further information on the fate and transport of organic chemicals in the environment can be found in the very useful practical guide by Ney (1995).

Table 10.13 Factors That Influence the Translocation, Transformation, and Persistence of Organic Chemicals and the Approximate Range or Rates That Describe These Environmental Processes

Property	Range in Organic Chemical Properties		
Water solubility (ws)	<10 mg/L	10–1,000 mg/L	>1,000 mg/L
Octanol/water (K_{ow})	>1,000	500–1,000	<500
Sorption (K_{oc})	>10,000	1,000–10,000	<1,000
Hydrolysis ($t_{1/2}$)	>90 days	30–90 days	<30 days
Photolysis ($t_{1/2}$)	>90 days	30–90 days	<30 days
Vapor pressure (torr)	<0.000001	0.000001–0.01	>0.01

Environmental Fate and Transport of Organic Chemicals (with properties listed above)

Soluble	Negligible	Variable	Yes
Hydrolyzes	Negligible	Variable	Yes
Photolyzes	Negligible	Variable	Yes
Volatilizes	Negligible	Variable	Yes
Adsorption potential	High	Intermediate	Low
Persistence potential	High	Intermediate	Low
Leaching potential	Low	Intermediate	High
Runoff potential	Low	Intermediate	High
Bioaccumulates	Yes	Variable	Negligible
Biodegradable	Slowly	Intermediate	Yes
Metabolized	Slowly	Intermediate	Yes

Source: Ney, R. E., *Fate and Transport of Organic Chemicals in the Environment: A Practical Guide*, 2nd ed., Government Institutes, Rockville, MD, 1995.

Example Problem 10.4

Compare and contrast the differences between the pesticide DDT and the solvent TCE based on the information below and Table 10.13.

DDT	solubility	=	0.002 mg/L	TCE	solubility	=	1100 mg/L
	K_{ow}	=	960,000		K_{ow}	=	195
	K_{oc}	=	238,000		VP _(vapor pressure)	=	58 torr
	high bioconcentration factor				photochemically sensitive		

Based on their organic chemical characteristics, DDT should be adsorbed, have a low runoff potential, and bioaccumulate, whereas TCE should have high leaching and runoff potential, can be biodegradable, could potentially volatilize, and possibly undergo photolytic transformation. Both chemicals can be environmental contaminants that may enter the food chain.

Environmental Quality Issues/Events

Rehabilitation of a Contaminated Wood-Preservative Site in Laramie, WY

Creosote is an oily, translucent, brown-to-black liquid with a sharp smoky or tarry odor that is a complex mixture of organic chemicals. Creosote is derived from coal tar and contains more than 250 organic compounds, of which about 85% are PAHs, 10% are phenolic compounds, and 5% are N-, S-, and O-heterocyclic compounds. Creosote and coal tar, which are denser than water (1.08 to 1.13 g/cm³), are *nonaqueous-phase liquids* (DNAPL) that can percolate beneath the groundwater table until an impermeable layer is reached. During the late 1970s, creosote solutions were used at approximately 188 of 631 wood-treating plants operating in the United States. Since 1980, more than 56 wood-preserving contaminated sites, most of which used creosote or *pentachlorophenol* (PCP), were listed on the EPA Superfund *National Priorities List* (NPL), with many of these located in the western United States. The *Union Pacific Railroad* (UPRR) Baxter tie-treating plant in Laramie, WY was one of these Superfund sites; however, unlike many Superfund cleanup projects, reclamation efforts at the Laramie Tie Plant have been totally funded by UPRR.

From 1886 to 1983 the UPRR managed the Laramie Tie Plant as a wood-preservative facility to treat railroad cross ties and snow fencing with creosote/oil and PCP/oil mixtures. Although creosote was the primary wood preservative, smaller amounts of PCP were also used for a limited time after 1956. Retort drippage and spills during wood-treatment operations and wastewater discharges into low-lying impoundments at the site resulted in the accumulation of the DNAPL mixture and contamination of surface soils, subsurface media, and groundwater. Unlike the many PAH compounds in creosote, PCP is more water soluble; PCP also has been detected in alluvium groundwater at the Laramie tie site. Because of the hazardous nature of the wastes associated with the past Laramie Tie Plant activities, cleanup of the site was authorized under both the EPA's *Resource Conservation and Recovery Act* (RCRA) and the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) programs.

The *Laramie Tie Plant* is located on the Laramie River floodplain. Geologically, the site consists of a thin surficial layer of recent alluvial deposits that directly overlie bedrock units. The alluvial sediments consist of silts, sands, and gravels that typically range from 1.5 to 4 m in thickness. The alluvial sediments are underlain by the Morrison formation confining sequence, which consists of siltstones, shales, and fine sandstones, and the Sundance formation that comprises fine- to medium-grained sandstone. The Sundance formation is a secondary aquifer, although high salt contents make the water unsuitable for most purposes. Fortunately, most subsurface contamination at the site is limited to the alluvial sediments, although the Morrison and Sundance formations do contain some DNAPL contamination.

The first step in the Laramie Tie Plant closure and cleanup process was to build a dike along the Laramie River to protect the site from a 100-year flood. In 1985, the Laramie River channel was realigned 50 m west of the site to permit the installation of a cutoff wall around a 140-acre area surrounding the contamination. Installation of a 3000-m-long soil/bentonite slurry cutoff wall was completed in 1987 to

prevent lateral migration of contaminants from the site. Construction of the cutoff wall involved digging a trench 1 m wide and approximately 5 to 25 m deep depending on the depth to bedrock. The cutoff wall is part of the multicomponent *contaminant isolation system* (CIS) that was designed to minimize contaminant migration from the site. The CIS includes a water management system that maintains water levels within the CIS area at levels below those outside the site to ensure that any lateral water movement will be into the site, and an activated C water-treatment plant that treats the contaminated groundwater from within the site.

In 1987, feasibility studies were conducted to evaluate several *remediation technologies* including subsurface oil recovery and different treatment options such as soil washing and *in situ* bioremediation of subsurface and surface soils. Soil washing effectively cleaned the coarser sediments, but generated fluids containing stable oil emulsions, high contaminant concentrations, and high salinity that were extremely difficult to treat. Also, the fine-textured sediments and impermeable zones were left untreated. The initial tests indicated bioremediation of contaminated subsurface materials using native, aerobic microorganisms had the potential to be an effective process. The main requirement for the technical feasibility of subsurface bioremediation was meeting the oxygen demand of the process. At a flow rate of 15 million L of oxygenated water per day, full-scale subsurface bioremediation was projected to require 250 years or more. Surface bioremediation reduced contaminant concentrations; however, much of the high-molecular-weight PAHs and PCP persisted. Surface bioremediation was estimated to require 20 years or more to clean up a 1.2-m-thick layer of soil.

The *water-flood oil recovery* technique was found to be an effective means for recovering subsurface DNAPL oil from the alluvial deposits. In a 1989 pilot test, more than 850,000 L of reusable preservative oil was recovered from a 1-ha subsurface area in 90 days. To date, water-flood oil recovery efforts have been successful in removing significant amounts of the DNAPL. The Laramie Tie Plant contamination included free DNAPLs and DNAPLs at immobile residual saturations, of which more than 8 million L have been recovered by the water-flood oil recovery process. After oil recovery efforts were completed in 2002, some of the DNAPL remains in the sediments beneath the site at immobile residual saturations. Equilibration of groundwaters with the remaining DNAPLs will maintain saturated aqueous concentrations of the contaminants. Groundwater pumped from within the CIS will therefore be treated and discharged for an indefinite period of time. Consequently, the contaminants at the site will be contained; however, the residual DNAPLs will continue to be a potential source of onsite groundwater contamination.

In June 1995, the EPA issued a final decision on the corrective actions recommended for the Laramie Tie Plant. A *Corrective Action Management Unit* (CAMU) was described that would consolidate the contaminated surface materials, in one area within the site. The proposed CAMU site would be the former location of the creosote/oil surface impoundments. Oil-contaminated concrete debris, 5000 m³ of contaminated soil from an area outside the CIS where PCP was used, and other small areas of contaminated soil will be excavated and transported to the CAMU site within the CIS. Eventually, a cap of impervious clay, synthetic material, or vegetation is expected to cover the surface impoundment area to prevent the infiltration of water. Much of the contamination will remain at the site after these reclamation efforts are completed; however, immobilization of the contaminants at the site will be ensured by the CIS and water treatment process.

In April 1998, the City of Laramie and UPRR signed a memorandum of understanding (MOU) to develop a *phytoremediation/greenbelt project* cooperatively that includes cost-effective site restoration and beneficial use of part of the Laramie Tie Plant site. In the original RCRA negotiation, *Wyoming Department of Environmental Quality* (WDEQ) and the EPA underscored the importance of eventual site cleanup, which suggests additional strategies such as phytoremediation should be implemented at the site. Phytoremediation is expected to assist in the cleanup of the contaminated soils, subsurface materials, and groundwaters by physical, chemical, and biological processes. Because plants utilize large amounts of water, vegetative transpiration could reduce the volume of groundwater that requires treatment, thus reducing costs associated with operating the CIS water treatment facility. In addition to increased water use, plants used in the phytoremediation project will reduce wind and water erosion and provide aesthetic and botanical components to the Laramie Tie Plant ecosystem.

Plants selected for the phytoremediation/greenbelt project (Figure 10.10) include trees, shrubs, grasses, and forbs that are adapted to Laramie's climate, can tolerate site conditions (e.g., contaminants, salts, soil properties), are perennial plant species, have phytoremediation capabilities, and include both shallow- and deep-rooted plants. Plants used in this project can enhance creosote and PCP degradation through increased microbial activity, particularly in the rhizosphere (area around the plant roots), improving aeration of the

site, which will allow for greater chemical and biological oxidation, plant uptake, metabolism or degradation of organic contaminants, and cometabolism via biodegradation of root exudates and other organic plant and microbial substances. Specific vegetation selected for the phytoremediation project includes cottonwood and willow trees; wild ryegrass and wheatgrass; and alfalfa, yellow sweet clover, and alsike clover. Other plant species will be planted primarily for improving aesthetics, botanical diversity, and stabilization of the site and will include sacaton and foxtail grasses; caragana, woods rose, buffaloberry, chokecherry, dogwood, and serviceberry shrubs; and Colorado blue spruce and Rocky Mountain juniper evergreen trees. Some areas will be irrigated to maintain adequate water needs and for fertigation when necessary. See Figure 10.10 for how the phytoremediation/greenbelt looks 5 years after initial site revegetation.

The great amount of effort and funds (more than \$50 million by the end of 2001) that have been and will continue to be expended (about \$400,000 per year after 2001) by UPRR at the Laramie Tie Plant represents more of an ideal than a typical case. Conclusions regarding the practicality of reclamation technologies employed at the Laramie site will probably be followed at similar sites in the United States. A large number of reclamation technologies have been field-tested at the UPRR Laramie tie treating plant. The field tests indicated that long-term containment (CIS including operation of water treatment facility) is a practical technology. Long-term containment will likely be the reclamation approach followed at similar sites in the United States. Because the Laramie site is enclosed in a soil/bentonite cutoff wall, testing of new remediation techniques at the site will assist in developing future technologies for site remediation without the risk of off-site contamination. Use of phytoremediation practices is expected to enhance the long-term cleanup efforts of the Laramie Tie Plant, with plants providing a natural approach to water use, erosion control, and contaminant reduction.

See <http://www.epa.gov/ORD/NRMRL/Pubs/1997/625R97009.pdf> for more information on wood-treating sites and their cleanup.



Figure 10.10 (Color figure follows p. 242.) Phytoremediation. Native vegetation growing on the Phytoremediation/Greenbelt located within the Union Pacific Railroad (UPRR) Tie Plant, Laramie, Wyoming. The Laramie Greenbelt was opened to the public in 2001 and includes a park, bike path, and walkway that run approximately 8 km along the Laramie River. A portion of the UPRR Tie Plant received a topsoil cover over the surface soils to prevent any exposure of the remaining low-level soil contamination. Although the site is considered protective of human health and the environment, continued monitoring of both the phytoremediation (use of plants) sites and the potential risks to wildlife will be conducted under RCRA by the Wyoming Department of Environmental Quality every 5 years.

10.5 ORGANIC CHEMICAL ANALYSIS

To characterize the mobility and fate of organic chemicals, we must be able to monitor the compound of interest and the substances derived from transformation processes that result in metabolites or degradative products. *Chemical analysis* is therefore an indispensable component of all environmental investigations dealing with the evaluation of risks associated with organic chemicals (see Chapter 13 for further discussion on risk assessment). Since the early 1960s, analytical techniques and instrument advances have enhanced our capabilities to examine, evaluate, and predict the fate, mobility, and even toxicity of numerous organic chemicals that are used by agriculture, industry, and for improving our everyday lives.

Because of the extensive number and types of organic chemicals that are utilized on a daily basis, the many new organic substances that are manufactured yearly, and the different materials that can potentially contaminate various environments, the following discussion is limited. Those interested in knowing more about these subjects should refer to the extensive literature related to organic analysis or consider courses in analytical, organic, and biochemistry. The basics involved in the sampling, processing, recognizing, and quantifying of organic chemicals are presented in the following sections. In addition to determining the specific organic chemicals, we should always characterize the general properties and parameters that are pertinent to the ecosystems being studied. These include pH, electrical conductivity (EC) or total dissolved solids (TDS), organic matter (OM) or dissolved organic carbon (DOC) contents, soil fertility (see Chapters 3 and 4), and other parameters specific to the ecosystem studied.

10.5.1 Sample Collection and Preparation

Although collection and preparation of soil and water samples were discussed in Chapter 4, samples analyzed for organic chemicals must be properly collected, preserved, and stored to maintain their integrity and to ensure *quality assurance/quality control* (QA/QC) throughout the analytical process. Certain samples may require additional steps to prepare them for analysis. If substances that interfere with the organic chemical analysis are present, they must be removed by purification methods, and if the organic chemical of interest is present at low levels, concentration methods must be used to increase the amount to above detection levels of the analytical technique employed. Soil and sediment samples generally require extraction of the organic chemicals, and because the various extraction methods used (e.g., acids, bases, solvents) tend to be nonselective, further cleanup and concentration are often required. Water samples can also be extracted using different solvents that are useful for concentration purposes (e.g., diethyl ether, *t*-butyl methyl ether, dichloromethane, and pentane). For soil and sediment samples, the use of *water-miscible solvents* (e.g., methanol, acetonitrile, dimethylformamide, and tetrahydrofuran) may be preferred because the organic chemical of interest can then be separated from the extracting solvent by using a water-immiscible solvent such as those used in extraction and concentration methods discussed above.

In addition to extraction and concentration procedures, cleanup and derivatization may also be required with some samples before the analytical quantification of the substance(s) of interest can be determined. Some of the methods employed for the cleanup step include chromatographic techniques (i.e., thin-layer, gel permeation, and ion-exchange), dialysis membranes, reverse osmosis, and supercritical fluid extraction. Water samples are usually the easiest to extract because the organic chemicals are already in solution. Use of water-immiscible solvents, purging (volatile compounds), activated charcoal, *hydrophobic resins* (e.g., XAD adsorptive resins), and various liquid chromatography methods can be used to separate and purify the organic chemicals of interest. Organic chemicals in soils and sediments are more difficult to separate and purify because of the numerous inorganic and organic substances in these samples. For samples with nonvolatile organic chemicals, freeze-drying can be used, whereas with volatile organic chemicals, anhydrous sodium sulfate may need to be added; both of these samples can be extracted with water-immiscible solvents

Table 10.14 Phenolic Compounds Identified in a Study Investigating Low-Molecular-Weight Organic Chemicals in Spodosol Hydrosequences and Developmental Sequences; Retention Times Given for Each Compound Were Determined Using HPLC with UV Detection

Compounds	Retention Time (min)
Benzoic Acids	
Protocatechuic acid (3,4 diOH) ^a	5.12
<i>p</i> -Hydroxybenzoic acid (4OH)	8.14
Vanillic acid (4OH, 3OCH ₃)	11.07
Benzaldehydes	
<i>p</i> -Hydroxybenzaldehyde (4OH)	9.25
Vanillin (4OH, 3OCH ₃)	14.31
Cinnamic Acids	
trans <i>p</i> -Coumaric (4OH)	24.48
Ferulic (4OH, 3OCH ₃)	34.29

^a Numbers and abbreviations in parentheses represent location and type of functional group arrangements on the organic chemicals.

Source: Adapted from Vance et al., 1985; 1986.

using a *Soxhlet apparatus* (e.g., reflux extraction of soluble constituents). A preextraction step may also be employed to remove the highly soluble, easily accessible organic chemicals, which can be combined with the Soxhlet-extracted materials before final analysis. Simple solvent extraction may be feasible for some samples with water-soluble organic chemicals of interest. For example, low-molecular-weight phenolic compounds in hydrosequences and developmental sequences of Michigan Spodosols were determined by extracting soils with sodium pyrophosphate (Na₄P₂O₇), acidifying the extracted solution to pH 2.5, followed by separating the phenolic organic chemicals using diethyl ether; Table 10.14 lists the organic compounds and their retention times determined in these studies. Identification of protocatechuic acid is especially noteworthy because of its ability to complex metal ions (e.g., Al³⁺ and Fe³⁺) and enhance metal translocation in soils.

10.5.2 Identification and Quantification of Organic Chemicals

Analytical methods commonly used for organic compound identification include gas chromatography (GC), high-pressure liquid chromatography (HPLC), mass spectrometry (MS), and GC-MS. Some additional analytical techniques that are used for specific studies on organic chemicals in environmental samples are ultraviolet (UV)-visible and infrared (IR) spectrophotometry and nuclear magnetic resonance (NMR). Some organic chemicals, e.g., neutral compounds, can be analyzed directly using GC, HPLC, or GC-MS, whereas organic chemicals with functional groups such as hydroxyl, carboxylic acids, amino, and carbonyl groups may require derivatization procedures. With HPLC, derivatization may be needed only if UV detection is used and the organic chemicals of interest do not absorb in the UV range. For MS, UV-visible, IR, and NMR methods, specific functional groups, C compound characteristics, and bonding arrangements may be deduced either directly or indirectly.

Organic chemicals can be characterized and quantified directly using UV-visible, IR, NMR, and MS methods; however, GC and HPLC separate organic substances, which are then analyzed and quantified using different types of *detection sources*. For GC a number of detectors are used, including flame ionization detection (FID) and electron capture detection (ECD), or the GC can be interfaced to an MS. The latter system can be extremely useful for the separation, characterization, and quantification of unknown organic chemicals if they are sufficiently volatile.

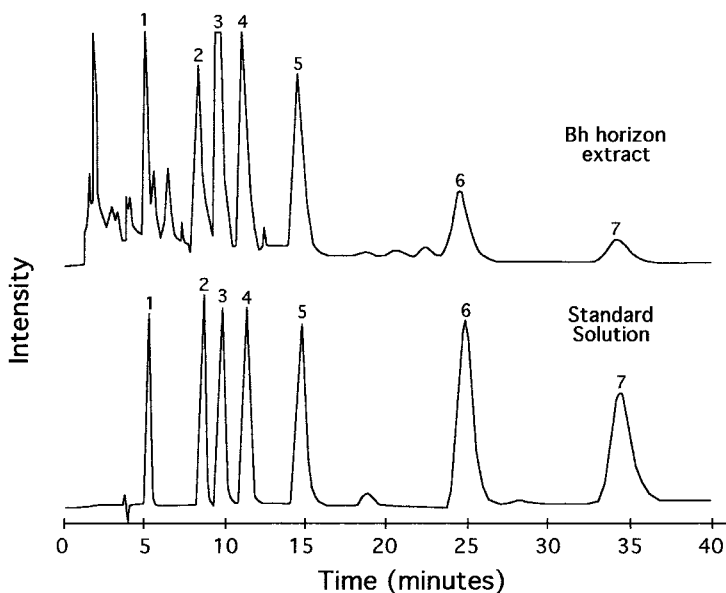


Figure 10.11 Typical high pressure liquid chromatography (HPLC) chromatograph of sample and standard solutions. (Adapted from Vance et al., 1985.)

However, because of the high cost of the instrumentation, GC-MS is not always available. FID and ECD detection are the two most common methods of detection with GC. FID detects a change in current flowing between two electrodes (polarizing and collector) placed in a flame when an organic compound is introduced. It is one of the most sensitive and widely used GC detectors, is sensitive to all organic compounds (10^{-12} g), and is not sensitive to inorganic compounds (e.g., H_2O , CO_2 , CO , N_2 , O_2). The EC detector is highly sensitive and detects organic compounds that capture electrons produced through the ionization of the carrier molecules by a beta source (β rays; see Chapter 9), which reduces the standing current. A major advantage of ECD is its selectivity and sensitivity (10^{-13} g) for organic halides and P and N compounds; compounds such as paraffins, simple hydrocarbons, amines, and alcohols are not electron-capturing species. For HPLC, several types of detectors are available, including UV-visible or fluorescence spectrophotometry and conductivity. An example of the use of HPLC with UV for detection of phenolic compounds extracted from soils is shown in Figure 10.11.

Once the organic compounds have been identified, the next step is to determine the concentration of the substance, i.e., quantify the amount present in the sample analyzed. A *standard sample* should be characterized within the same batch of samples of unknowns to verify the specific compound is present and, with multiple standards of different concentrations, to ascertain the concentration in the sample analyzed. By using several standards, many instruments can be calibrated to measure the concentration of the unknown organic chemical directly. If an instrument cannot be calibrated, results such as peak area, peak height, absorption, fluorescence, and conductivity for the instrument utilized can be evaluated using a computer spreadsheet to develop standard curves that calculate concentrations of the organic chemical of interest.

10.6 ALTERNATIVE PEST MANAGEMENT AND PLANT BREEDING STRATEGIES

Most people would agree that pest control is usually managed by using various types of organic pesticides. *Integrated pest control programs*, however, rely on a combination of biological, chemical, mechanical, and cultural controls to provide economic, ecological, and sociological benefits as we manage pest populations. Alternatives to the use of pesticides for controlling certain insects and

weeds have gained popularity in recent times because they can require less input and be more sustainable. Two approaches utilized to reduce our dependence on pesticides include biological control and genetically modified crops. In addition, genetically modified crops may possess cold temperature hardiness, result in greater yields, contain higher nutrient contents, as well as other traits that are often bred into plants through conventional methods.

10.6.1 Integrated Pest Management

In the last few decades, there has been an emphasis on reducing pesticide use, with some insecticides that represent the greatest risk to humans and environmental health losing their registrations and being withdrawn from use. Because of these concerns, integrated pest management, also known as IPM, programs of pest control have been developed that rely on several practices to prevent pest outbreaks from occurring. Preferably, these practices should be compatible and each should augment the effectiveness of the other. Some of the components of an effective IPM program are soil preparation for the control of pests (weeds, microorganisms, and insects), chemical (pesticides) and biological pretreatment of soils for the control of weeds and insects, observations of pest activities both locally and regionally, better time management strategies, and understanding climatic conditions that are conducive to pest outbreaks.

The two most important principles associated with IPM are (1) integration of several different practices that are compatible, and (2) using economic pest-density thresholds, so that costly pesticides are only used when pest densities are high enough to incur major economic loss. A practice related to the second principle is based on pheromone mate disruption. Part of the reason for this success is that insects send out chemical signals called pheromones to communicate with other members of their species. In general, adult females produce a particular pheromone that attracts only adult males of their species. Synthetic *sex pheromones* are known to attract adult moths of the beet armyworm, black cutworm, cabbage looper, corn earworm, diamond-back moth, fall armyworm, potato tuberworm, tomato pinworm, and variegated cutworm. Pheromone traps have been used to trap certain pests in fruit trees such as the Oriental fruit fly in Hawaii. Mating disruption with synthetic sex pheromones is used against some pests of fruit and forest trees.

In an IPM program, several practices must be followed to prevent pest problems, including the use of *certified disease-, weed-, and insect-free seeds or plants*; implementation of cultural practices such as crop rotation and sanitation measures; control of physical conditions (time of tillage, planting conditions, temperature and moisture of storage conditions for the prevention of diseases); utilization of chemical practices (pesticides, fumigants, seed and plant treatments, and use of disinfectants); and development of innovative biological control practices such as use of insect- and disease-resistant varieties (see the next sections for additional discussion on biological control and use of genetically modified crops). Individually, these practices may not provide adequate protection for pest control; however, collectively these practices can minimize economic losses due to pest problems.

Integrated pest management programs are becoming more accepted within the agricultural production sector as individuals gain a greater understanding and appreciation of how nature works and as the concern for environmental quality grows. Conservation tillage practices, such as no-till, are used because they generally result in a reduction in soil loss due to wind and water erosion and an increase in the amount of water retention when crop residues are left on the soil surface. However, as this alternative agricultural practice increases, problems associated with increased occurrences of weed, disease, insect, nematode, and rodent problems will require additional attention in an IPM program. Consequently, *biological control* measures, use of resistant varieties, or altered cultural practices may be needed along with pesticide applications to combat the problems developed by conservation tillage systems. In addition, as organisms become immune to pesticides, other forms of control, new and improved chemical treatments, and alternative plants such as transgenic Bt crops (plants cloned with *Bacillus thuringiensis* protein gene) must be evaluated for their sustainable contribution to agricultural production.

10.6.2 Biological Control

Humans are primarily responsible for the dissemination of insects and weeds throughout the world. Many of the most troublesome weeds and insects in the United States, i.e., Russian thistle, St. John's wort (Klamath weed), johnsongrass, gypsy moth, screw worm, and Russian wheat aphid, to name a few, are a result of travel and commerce activities. Weeds and insects from exotic countries may proliferate if (1) they adapt to the new environment and (2) their natural enemies are not present. One approach for moderating weed and insect populations is to introduce biological control agents from the pest's native region that can reduce or regulate the pest to a level that is economically, aesthetically, or environmentally acceptable. Natural enemies have been successfully introduced to combat exotic insects and weeds that have displaced the native plant or insect species.

Biological control (e.g., biocontrol) is an alternative to pesticide use that relies upon *natural enemies* to suppress pest populations. Biocontrol is just one component of IPM and is based on the reduction of pest populations by natural enemies either through introduction by humans or present as indigenous species (Hoffmann and Frodsham, 1993). Natural enemies of insect pests, also known as biocontrol agents, include predators, parasitoids, pathogens, and insect diseases; biocontrol agents of weeds include insects, pathogens, and herbivores. Predators are primarily free-living species such as lady beetles and lacewings that spend their lives consuming large numbers of prey. Parasitoids include species of wasps and some flies that develop during their immature stage on or in an insect host, often resulting in the death of the host. Pathogens are bacteria, fungi, and viruses that are disease-causing organisms that kill or debilitate their host; pathogens are relatively specific to certain insect groups. More successes have been achieved with the control of insects than weeds using biocontrol.

Biocontrol can be an effective alternative to pesticide use, with an ideal biocontrol program resulting in pest populations maintained at levels below which economic losses occur and without placing undue stress on the ecosystem. Successful biocontrol of pests can be accomplished on a small scale as well, such as in gardens or on small farms. Hoy (1989) summarized the three most commonly employed biocontrol strategies, which are listed in Table 10.15 and discussed below.

Classical biological control is often used when an insect or weed is accidentally introduced into a new geographic area without its associated natural enemies (Table 10.15). Classical biocontrol can be long-lasting and inexpensive, and other than the initial costs of collection, importation, and rearing, little expense is incurred. Classical strategies involve the importation and release of natural enemies to control introduced (exotic) pests and sometimes native pests; however, biocontrol is usually more effective against exotic rather than against native insect pests. First, the origin of the exotic pest must be determined in order to collect natural enemies associated with the pest. Second, the natural enemy must go through a rigorous quarantine process, to ensure that no unwanted organisms are introduced. Third, the natural enemies must then be reared, usually in large numbers,

Table 10.15 Biological Control Strategies for Controlling Insect and Weed Pests

Biological Control Strategy	Description	Impacts/Concerns
Classical	Importation and establishment of exotic natural enemies to control exotic pests and occasionally native pests	Introduced exotics comprise about 40% of the insect pests in the United States; many examples of successful control of pests
Conservation	Actions to protect, maintain, and/or increase the effectiveness of natural enemies	Importance of natural enemies not adequately studied; insecticide often indiscriminately reduces or eliminates natural enemies
Augmentation	Activities include increases in populations or beneficial effects of natural enemies, which may not be self-sustaining	Requires planned releases at critical time of the year or release of large numbers of natural enemies; habitat modification

and released in the area of the pest. Finally, follow-up studies must be conducted to determine if the natural enemy (Table 10.16) has successfully established at the site of release. Once a natural enemy is successfully established, little or no additional input is needed.

Examples of successful classical biocontrol programs include the use of the vedalia beetle (*Rodolia cardinalis*) and a parasitoid fly from Australia to control the cottony cushion scale (*Icerya purchasi*) that threatened the livelihood of the California citrus industry in the 1880s. It took only a few years before the cottony cushion scale was completely controlled by the introduced natural enemies. Other pests that were at least partially controlled by beneficial insects include the European corn borer (*Ostrinia nubilalis*), which is one of the most destructive insects in North America, European spruce sawfly (*Diprion hercyniae*), and Oriental fruit fly (*Dacus dorsalis*). A small wasp, *Trichogramma ostrinae*, from China was introduced to help control the European corn borer. After introduction of several natural enemies of the alfalfa weevil, an introduced pest of forage, infested land in the northeastern United States that was treated for alfalfa weevil was reduced by 75% within 20 years. Numerous classical biocontrol programs for insect pests and weeds are currently under way across the United States and Canada.

Conservation biological control relies on the conservation of natural enemies to prevent loss from insect and weed pests (Table 10.15). This strategy is considered the most significant and attainable biocontrol practice available because conservation of natural enemies is generally cost-effective and relatively simple. Examples of conservation biocontrol include lacewings, lady beetles, and hover flies that feed on aphids and fungi that infect adult flies under high humidity conditions (Table 10.16). Because natural enemies occur in all production systems, they may easily be adapted to the local environment and to the target pest(s). With relatively little effort, the activity of natural enemies can be identified and their conservation can be enhanced with the use of cover crops or intercropping practices, for example. Factors associated with enhancing natural enemy habitats will increase their preservation and well-being, while minimizing negative impacts. Greater efforts need to be made to conserve and consider the importance of natural controls when making pest management decisions (Pickett and Bugg, 1998).

Augmentation biological control involves either (1) supplemental releases of natural enemies or (2) manipulation of the natural enemies' habitat (Table 10.15). Releases may be done at certain times (inoculative release) of the season or they may include large numbers (inundative release). Augmentation biocontrol is often used in the production of different crops grown in greenhouses, although frequent release of large numbers of parasitoids is also a commonly used practice in greenhouses. Some examples of augmentation biocontrol include releases of the parasitoid *Encarsia formosa* for control of greenhouse whiteflies and of the predaceous mite *Phytoseiulus persimilis* for control of the two-spotted spider mite. Often large numbers of lady beetles, lacewings, and parasitoids such as *Trichogramma* are released (Table 10.16). In vegetable or field crops, the number of individuals released is dependent on the level of pest infestation and can range from 2,000 to 100,000 per hectare per week. Even enormous numbers (e.g., millions and even billions per hectare) of nematodes have been released to control certain soil-dwelling insect pests. The second approach to augmentation biocontrol involves changing the cropping system to augment the natural enemies' effectiveness. An example of habitat manipulation includes growing plants to attract and maintain populations of natural enemies close to crop production areas. This strategy works well in gardens and small-scale commercial operations.

Biocontrol has also been successfully used to control certain terrestrial and aquatic weeds. The biocontrol of the common prickly pear (*Opuntia inermis*) and spiny prickly pear (*O. stricta*) in Australia and St. John's wort or Klamath weed (*Hypericum perforatum*) in the United States are classic examples of terrestrial weed control by beneficial insects that feed on these weed species and not on agronomic plants. Herbivorous, e.g., white amur (*Ctenopharyngodon idella*), and non-herbivorous, e.g., carp (*Cyprinus carpio*), fish have been found to control aquatic weeds either by consumption or by uprooting them, respectively. Several examples of weeds common to the western United States and biocontrol agents showing promise in their control are listed in Table 10.17.

Table 10.16 Common Types of Natural Enemies Used in Biological Control of Insect and Mite Pests

Natural Enemy	Feeding Habits/Comments
Predators	
Lady beetles (<i>Coccinellidae</i>)	Adults and larvae feed on aphids, spider mites, insect eggs, and other soft-bodied insects; adults commonly colonize annual crops where suitable prey are present; several species commercially available
Ground beetles (<i>Carabidae</i>)	Adults and larvae generalist feeders on insects in and on soil; some feed on weed seeds; common in crop borders but cultivation limits abundance in crops
Rove beetles (<i>Staphylinidae</i>)	Adults and larvae feed on insects in and on soil including seed corn maggot and onion maggot; common in crop borders
Green lacewings (<i>Chrysopidae</i>)	Larvae feed on aphids, small caterpillars, and beetles; adults feed primarily on nectar; adults commonly colonize annual crops; several species commercially available
Syrphid flies (<i>Syrphidae</i>)	Larvae feed on aphids and other soft-bodied insects; adults feed on flowers
Predatory bugs (<i>Hemiptera</i>)	"Beak" is used to pierce prey and suck out body fluids
Stink bugs (<i>Pentatomidae</i>)	Adults and nymphs of some species feed on insects including the Colorado potato beetle; some species are plant feeders
Damsel bugs (<i>Nabidae</i>)	Adults and nymphs feed on insects especially caterpillars and aphids; sometimes common in crops
Minute pirate bugs (<i>Anthocoridae</i>)	Adults and nymphs feed on thrips, spider mites, and insect eggs; sometimes common in crops; commercially available
Predatory mites (<i>Phytoseiidae</i>)	Feed primarily on spider mites; commercially available; fairly widespread, successful use as augmentative biocontrol agents in greenhouses and some outdoor crops
Spiders (<i>Araneae</i>)	Abundant generalist feeders on insects; hunt for prey on soil and plants or use webs to trap prey; often habitat specialists; very important as "natural" biocontrol agents
Parasitoids	
Tachinid flies (<i>Tachinidae</i>)	Females parasitize moths, beetles, sawflies, and other insects in diverse habitats; individual species often have highly restricted host ranges; often used in classical biocontrol

continued

Table 10.16 Common Types of Natural Enemies Used in Biological Control of Insect and Mite Pests (continued)

Natural Enemy	Feeding Habits/Comments
Parasitic Wasps	
Braconid wasps (<i>Braconidae</i>)	Females parasitize a diverse array of arthropods including most of the important pest groups; also kill hosts through host feeding; diverse habitats; individual species often have highly restricted host ranges; extensively used in classical biocontrol; some commercially available for augmentation biocontrol
Ichneumonid wasps (<i>Ichneumonidae</i>)	
Chalcid wasps (<i>Chalcidoidea</i>)	
Insect Diseases	
Viruses	Most common hosts are moths, butterflies, sawflies, and beetles; often highly host-specific; some successfully used in classical and augmentation biocontrol; viral epidemics widespread in nature
Bacteria	Several bacteria (primarily <i>Bacillus</i> sp.) have been extensively researched for control of caterpillars, beetles, and mosquitoes; <i>B. thuringiensis</i> ("Bt") is the most notable and is sold commercially for caterpillar and mosquito control; genes coding for a toxic protein in Bt have been transferred to several crop species to provide constitutive defense against insect attack
Fungi	Infect a broad array of pest arthropods; "natural" outbreaks common; limited commercial availability to date for augmentative releases
Nematodes	Kill hosts by internal feeding or through mutualistic bacteria that cause septicemia in host; some species have broad host ranges and are used in augmentation biocontrol; others have more restricted host ranges and have been used in classical biocontrol
Protozoa	Includes species of <i>Nosema</i> , microsporidians that have been formulated in baits for control of locusts and grasshoppers

Source: Van Driesche, R. G. and Bellows, T. S., *Biological Control*, Chapman & Hall, New York, 1996.

Table 10.17 Some Biological Control Agents That Show Promise for Weed Control in the Western United States

Weed	Bioagent	Feeding Habit and Damage
Canada thistle	<i>Ceutorhynchus litura</i> <i>Urophora cardui</i>	Weevil larvae mine leaves, stem, root crown, and root reducing overwintering survival Galls formed by fly larvae in stems act as metabolic sink
Diffuse and spotted knapweeds	<i>Agapeta zoegana</i> <i>Cyphocleonus achates</i> <i>Larinus minutus</i> <i>L. obtusus</i> <i>Sphenoptera jugoslavica</i> <i>Urophora affinis</i> <i>U. quadrifasciata</i>	Moth larvae mine roots killing small plants and reducing flowering in larger plants Weevil larvae mine and gall vascular root tissue reducing plant vigor Weevil larvae feed in seedheads reducing seed production Beetle larvae mine gall roots depleting carbohydrate reserves Fly larvae gall or feed in seedhead reducing seed production
Goose	<i>Apion ulicis</i> <i>Tetranychus lintearius</i>	Weevil larvae eat seeds, adults eat foliage, mites pierce and extract cell contents from spines and stems
Leafy spurge	<i>Apthona lacertosa</i> <i>A. nigricutis</i> <i>Spurgia esulae</i>	Beetle larvae feed on root hairs and young roots reducing storage of reserves and water/nutrient uptake Midge larvae feed and gall growing tips reducing flower and seed production
Musk thistle, Italian thistle, plumeless thistle, Scotch thistle	<i>Rhinocyllus conicus</i> <i>Trichosirocalus horridus</i>	Weevil larvae consume developing seeds in head Weevil larvae feed on growing tip of rosette killing weak plants or main stem of healthy plants
Rush skeletonweed	<i>Cystiphora schmidtii</i> <i>Eriophyes chondrillae</i> <i>Puccinia chondrillina</i>	Midge larvae feed on stems and leaves reducing photosynthesis and flowering Galls form where mite feeds on buds resulting in plant death, stunting, or reduced seed production Rust fungus infects all aboveground plant parts resulting in plant death, reduced photosynthesis, or stunting of stems
St. John's wort	<i>Agrilus hyperici</i> <i>Chrysolina quadrigemina</i> <i>C. hyperici</i>	Beetle larvae tunnel inside root killing most plants Beetle larvae defoliate plants resulting in reduced foliage and root reserves
Tansy ragwort	<i>Longitarsus jacobaeae</i> <i>Pegohylemyia seneciella</i> <i>Tyria jacobaeae</i>	Beetle larvae mine rosette roots and adults feed on leaves often killing the plant Fly larvae consume seeds in developing seed heads Moth larvae strip foliage and destroy flowers

Source: Rees, N. E. et al., *Biological Control of Weeds in the West*, Western Society of Weed Science, Bozeman, MT, 1996.

10.6.3 Genetically Modified Crops

Selective breeding using *genetic engineering* has allowed researchers to develop crops with beneficial traits (e.g., improve yield, pest resistance, increase nutritional benefits, reduced environmental impacts). The use of *genetically modified* (GM) crops has also been questioned for several reasons including the potential of the GM crop in becoming an invader, hybridization with GM crop relatives resulting in the transfer of genes, or loss of biodiversity when using GM crops. It is important to remember that all traits of living organisms are the result of genes, which are segments of deoxyribonucleic acid (i.e., DNA) that code for specific proteins involved in the regulation of such activities that govern growth, color, height, and survival.

Selective plant breeding has been ongoing for years. Since the beginning of agriculture some 10,000 years ago, plant selection has resulted in crops with increased yields, disease resistance, and greater productivity. Corn, for example, originally had only a few small seeds per cob, but in time humans have selectively propagated plants with improved traits such as larger kernels, more kernels per cob, and stronger kernel attachment for better harvesting.

Traditional plant breeding involves the transfer of numerous genes from one generation to the next, including genes with beneficial as well as undesirable traits. Obtaining a desirable trait could thus take years to display its properties. A GM crop (Table 10.18) has genes that are altered by recombinant techniques that transfer a gene of interest from one organism to another. Therefore, in one growing season, plants can be genetically engineered to manifest beneficial traits. Because all living organisms have genes that code for similar proteins and properties, *gene transfers* can be done between plants or from organisms other than plants (e.g., fish genes transferred to strawberry plants).

The first GM crop was developed in 1983 and was a tobacco plant that exhibited a resistance to antibiotics. In the early 1990s, a delayed ripening GM tomato, “Flavr-savr,” was commercially released. Shortly afterward *glyphosphate-resistant* (Roundup Ready®) soybeans and corn were released (Roundup is a broadleaf herbicide); these two plants are the most common GM crops

Table 10.18 GM Crops, Altered Traits, and Extent of Production in the United States

Crop	Modified Traits	Hectares (% of total) of GM Crops Grown in the United States during 2002 or 2003
Canola	Herbicide resistance, modified oil, vitamin E enriched	0.33×10^6 ha (54%)
Cassava	Detoxification of cyanogens	Rarely produced
Coffee beans	Caffeine-free	None grown in Hawaii
Corn	Herbicide and insect resistance, male sterile, detoxification of mycotoxins	12.8×10^6 ha (40%)
Cotton	Herbicide and insect resistance	4.3×10^6 ha (71%)
Flax	Herbicide resistance	Unknown
Papaya	Virus resistance	53% of Hawaii's production
Potato	Insect resistance	Limited production
Rice	Provitamin A enriched, iron fortification	Unknown
Soybean	Herbicide resistance, modified oil	24.2×10^6 ha (81%)
Squash	Virus resistance	Limited production
Sugar beet	Herbicide resistance	Not widely adopted
Tomato	Insect resistance; modified fruit ripening; β -carotene, lycopene enriched	Limited production

grown in the United States. Since their initial release, corn and soybeans have been modified for resistance to pests, diseases, and even herbicides that are used to control weeds that compete with these two crops (see Table 10.18). Other GM crops have also benefited from added traits that have resulted in better plant health. Growers have gained by needing fewer inputs such as herbicides, insecticides, or chemicals to prevent diseases to produce their crops.

All foods containing any genetically altered plant or animal materials are classified as GM foods. Currently, GM foods comprise greater than 60% of the foods we buy in the supermarket. It is not surprising that most GM foods contain either GM corn or soybeans products such as starch, oils, proteins and other ingredients. Recently, a GM variety of rice, termed “golden rice” was developed that contains higher levels of β -carotene, a precursor for vitamin A. Because more than half the population of the world relies on rice as their primary food, with many of these individuals often malnourished, use of “golden rice” could have enormous benefits worldwide.

What are some other potential benefits that we may derive from utilizing GM? We can increase food production and agricultural profit by improving yields. We can improve food nutritional quality as well as increase the health benefit compounds they contain. We could improve on fresh fruit and vegetable storage, shelf life, and quality. We might be able to decrease problems associated with food allergenic compounds. We may even be able to develop crops that can be used as vaccines and other medical benefits. And, finally, we might be able to produce GM crops that can clean up polluted soils and waters, an innovative approach to ameliorating degraded environments. The future may be promising, but we need to be cautious as we move into the new frontier of genetic engineering.

PROBLEMS

- 10.1 List ten products that you use daily that contain organic chemicals. Based on what you have learned in this chapter, describe how the extraction, manufacturing, and/or processing of these materials may affect environmental quality.
- 10.2 Draw the chemical structures of known hydrocarbon compounds that are classified as alkanes, alkenes, and alkynes. Indicate the use of each compound and if it possesses potential environmental quality concerns.
- 10.3 What are the most probable causes of adverse effects of organic chemicals? What are some potential adverse effects due to natural causes that have affected the atmosphere, surface waters, and groundwaters?
- 10.4 Pharmaceuticals and endocrine disruptor chemicals are classified as “emerging risk” issues. Based on what you know of the potential harm that these substances may cause, and your daily or occasional habits, describe what you could do to minimize their introduction into the environment.
- 10.5 Human health issues involving organic chemicals have become more prevalent since the 1950s. Why are human health issues becoming more important as we develop new organic chemicals?
- 10.6 A 2-L bottle of liquid benzene (density of 0.76 g/mL) accidentally falls and breaks in a small 150-m³ laboratory that is not equipped with an air exchanger. Assuming the benzene evaporates completely, what would be the final concentration and the consequence to anyone working in the laboratory? See Example Problem 10.1 for additional information.
- 10.7 Soil microorganisms are important in the degradation of organic chemicals. How do certain types of soil microorganisms assist in the bioremediation of organic chemical-contaminated sites?
- 10.8 The K_{ow} can be used to predict the expected bioconcentration of an organic chemical that preferentially accumulates in organisms such as fish. Determine the level of DDT, in mg/kg, that would be bioconcentrated in the fatty tissue of fish if the surface water concentration for DDT was 0.000003 mg/L. Use Equation 10.7 and the K_{ow} for DDT of 960,000 to answer this question.
- 10.9 Determine the amount of material remaining after ten half-life ($t_{1/2}$) periods for an organic chemical that hydrolyzes and has a $t_{1/2}$ of 2 days and an initial concentration of 100 mg/kg.
- 10.10 Figure 10.7 illustrates the variation in Henry’s law constants for several classes of organic chemicals. Using Equation 10.5, determine which of these groups of organic chemicals are preferentially distributed in the aqueous phase. Explain why.

- 10.11 The half-life photolysis rates of organic chemicals in surface waters can determine the potential bioaccumulation, volatilization, adsorption, and other reactions. Assuming only photolysis to be important, determine the concentration of malathion that would be expected after 60 days if 1 kg was accidentally spilled in a pristine pond.
- 10.12 Parathion was detected in a landfill site at a soil solution concentration of 2 mg/L. If the soil tested had an organic C content of 3% and the K_{OC} of parathion is 4800, what would be the expected level of parathion adsorbed?
- 10.13 Characterize the beneficial effects that can be obtained when using plants to remediate an organic chemical-contaminated site. What are some disadvantages to the use of plants in areas with ground-water that contains organic contaminants?
- 10.14 In March 1989, the *Exxon Valdez* tanker ran aground in Prince William Sound, AK and released approximately 41 million L of crude oil that polluted 2200 km of Alaskan coastline. Of the methods used to clean up the contaminated beaches, fertilization with N and P was found to be the most successful. Explain why nutrient addition is sometimes needed in the remediation of organic chemicals and how N and P were useful for cleanup of the *Valdez* oil spill.
- 10.15 Pest management is an essential part of agricultural production. Although pesticides are widely used to control pests, other practices can reduce or eliminate the use of these materials. Describe three examples of alternatives to pesticide use.
- 10.16 It is not surprising that consumers are generally unaware of the use of biotechnology in foods, according to a USDA consumer focus group survey. The survey found that consumers viewed biotechnology as primarily a benefit to producers and manufacturers, had little concern for consumers, worried about long-term health effects, and believed there would be an impact on the environment. Therefore, it is apparent that clear, unambiguous information about biotechnology be developed and distributed in order to debate the merits and shortcomings of this technology. In your own words present a case as either an advocate or opponent to the use of biotechnology in modern-day agriculture.

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CHAPTER 11

The Atmosphere: Global Climate Change and Acidic Deposition

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11.1 INTRODUCTION

“*Air pollution* is the presence of any substance in the atmosphere at a concentration high enough to produce an objectionable effect on humans, animals, vegetation or materials, or to alter the natural balance of any ecosystem significantly” (Wolff, 1999). Based on this definition, air pollution can be the result of solids, liquids, or gaseous materials. Air pollution has been a constant natural occurrence since the formation of the Earth; however, only during postindustrial times have humans affected the atmosphere on a global scale. Initially, air pollution problems

that resulted from human activities were localized, but as human population growth increased, industrialization and natural resource utilization have resulted in impacts to our atmosphere as well as hydrosphere, biosphere, and terrestrial environments. Chapter 2 describes the general properties of our atmosphere, as well as pollutant issues and impacts such as those related to the stratosphere ozone layer. This chapter evaluates important phenomena related to anthropogenic changes in the atmosphere that influence regional, national, and global climatic conditions and atmospheric chemistry. Sources, impacts, and causes of two types of airborne pollution that have been major issues during the past 40 years are examined. We present details on atmospheric conditions that have resulted from human activity (e.g., global climate change and acidic deposition) and that have numerous effects and interrelationships with soil, plant, and aquatic ecosystems.

11.2 THE CLIMATE AND GLOBAL CLIMATE CHANGE

We often describe the climate for a given location as the net effect of a number of easily measurable characteristics such as maximum and minimum temperature, wind speed and direction, precipitation patterns, cloud type and amount, and solar radiation. These parameters have profound effects on humans, animals, and vegetation. The climate is also influenced by less obvious factors such as large-scale ocean currents, the vertical structure of the atmosphere, vegetation, soil moisture, and the albedo at the surface of the Earth. The atmosphere is influenced by the oceans, biosphere, cryosphere (glaciers, polar ice, etc.), and, to a lesser extent, by the geosphere. The climate system is extremely complex and is influenced by many factors and interactions.

The prospect of global climate change comes from the phenomenon known as *global warming*. Global warming refers to the possibility that the global average air temperature may be increasing because the concentrations of various gases in the atmosphere are also increasing (see Chapter 2). These gases create the *greenhouse effect*, which allows the atmosphere to trap radiant energy that would otherwise radiate freely away from the Earth, and therefore allows the atmosphere to retain heat and maintain a temperature suitable for life. In fact, the greenhouse effect allows life as we know it to exist. Without the greenhouse effect, the surface of the Earth would be approximately 33°C (~60°F) colder than it is now. Global warming is often referred to as the greenhouse effect when in reality global warming represents an enhancement of the greenhouse effect. The *anthropogenic greenhouse effect* would be a more appropriate term for global warming.

11.2.1 The Greenhouse Effect and Evidence of Global Warming

The wavelength of maximum emission for incoming solar radiation is 0.48 μm , representing a relatively high energy level. Conversely, the infrared emission from the surface of the Earth has a wavelength of maximum emission of approximately 9.7 μm , representing a much lower energy level. Some incoming solar radiation has sufficient energy to pass through the atmosphere, but the reemitted infrared radiation, measured as heat, is absorbed by greenhouse gases, and the energy becomes trapped in the atmosphere. The gases that absorb the infrared radiation are called radiatively active gases. The higher the concentration of the greenhouse gases, the more heat is trapped. A simple example of the greenhouse effect can be found in an automobile parked outside on a sunny day with the windows closed. High-energy solar radiation passes through the glass and warms the interior surfaces. These surfaces then transfer that heat to the air inside the automobile and the warm air is trapped by the glass. The greenhouse gases act as the glass in our automobile example and trap some of the heat in the atmosphere. The mechanisms by which the air is heated in the automobile are slightly different from those in the atmosphere. In the automobile, most of the heat is transferred by the air directly contacting

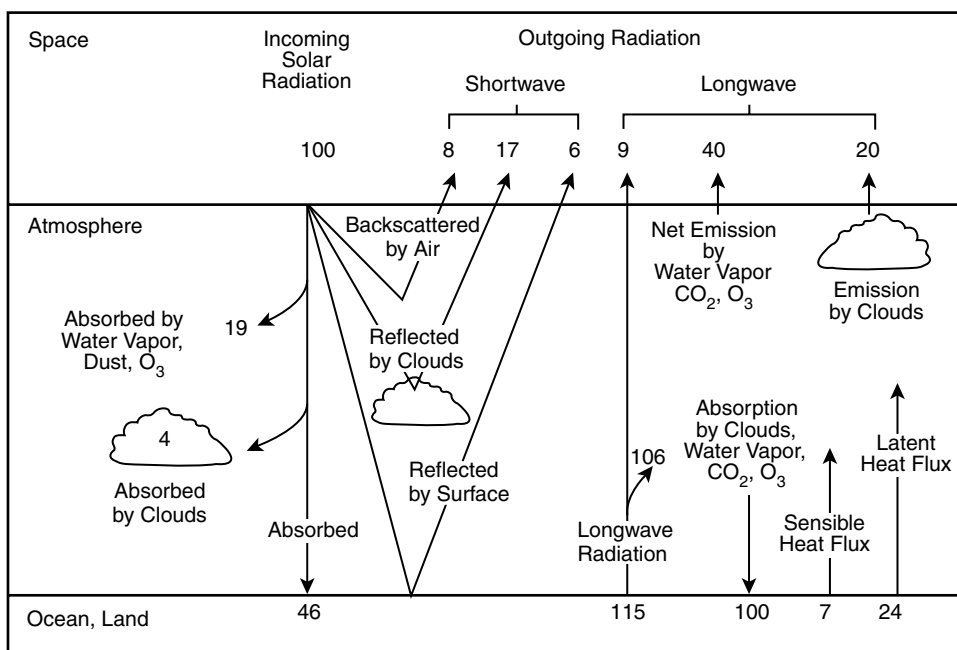


Figure 11.1 The global energy balance in units of percent incoming solar radiation. (From MacCracken and Luther, 1985.)

the warm surfaces, whereas in the atmosphere the gases absorb the emitted infrared radiation to warm the air (although direct transfer of heat to the air also occurs in the atmosphere). Infrared radiation travels an average of approximately 1 km in the atmosphere before it is absorbed by greenhouse gases.

The greenhouse effect can be shown from the global energy balance depicted in Figure 11.1. As shown in the figure, 100 units of incoming solar radiation enter the atmosphere and 31 units are reflected to space; 46 of the remaining units are absorbed by the surface and are partly used to heat the atmosphere directly (sensible heat flux) and to evaporate water (latent heat flux). The surface of the Earth emits 115 units of infrared radiation, which is greater than the incoming solar radiation, and is evidence that the Earth is still a cooling body. The fact that 100 units of infrared radiation are emitted downward from the atmosphere to the surface from absorption by clouds, water vapor, carbon dioxide (CO₂), and ozone (O₃), in addition to the 46 units absorbed by the surface directly from incoming solar radiation, allows the surface to warm more than it would by incoming solar radiation alone. The anthropogenic greenhouse effect causes an increase in the flux of infrared radiation downward to the Earth's surface.

The most obvious indication that global warming is occurring would be changes in temperatures in the troposphere. The mean global temperature is the mean of the mean annual temperature for a number of locations distributed across the Earth. The mean annual temperature for a given location is the mean of the high and low temperatures for each day of the year. In 1998, the warmest year on record, the average surface temperature of the whole planet was 14.0°C (57.2°F). The average temperature was slightly warmer in the Northern Hemisphere (14.6°C or 58.3°F) with a greater landmass, and a little cooler (13.4°C or 56.1°F) in the Southern Hemisphere where there is more water. It is clear that the global mean temperature, as compared with the 30-year average from 1961 to 1990, has increased recently, as shown in Figure 11.2. Temperatures have increased approximately 0.6°C (1.1°F) in the last 100 years and the four warmest years on record have all occurred since 1998 (1998, 2002, 2003, and 2001 in descending order).

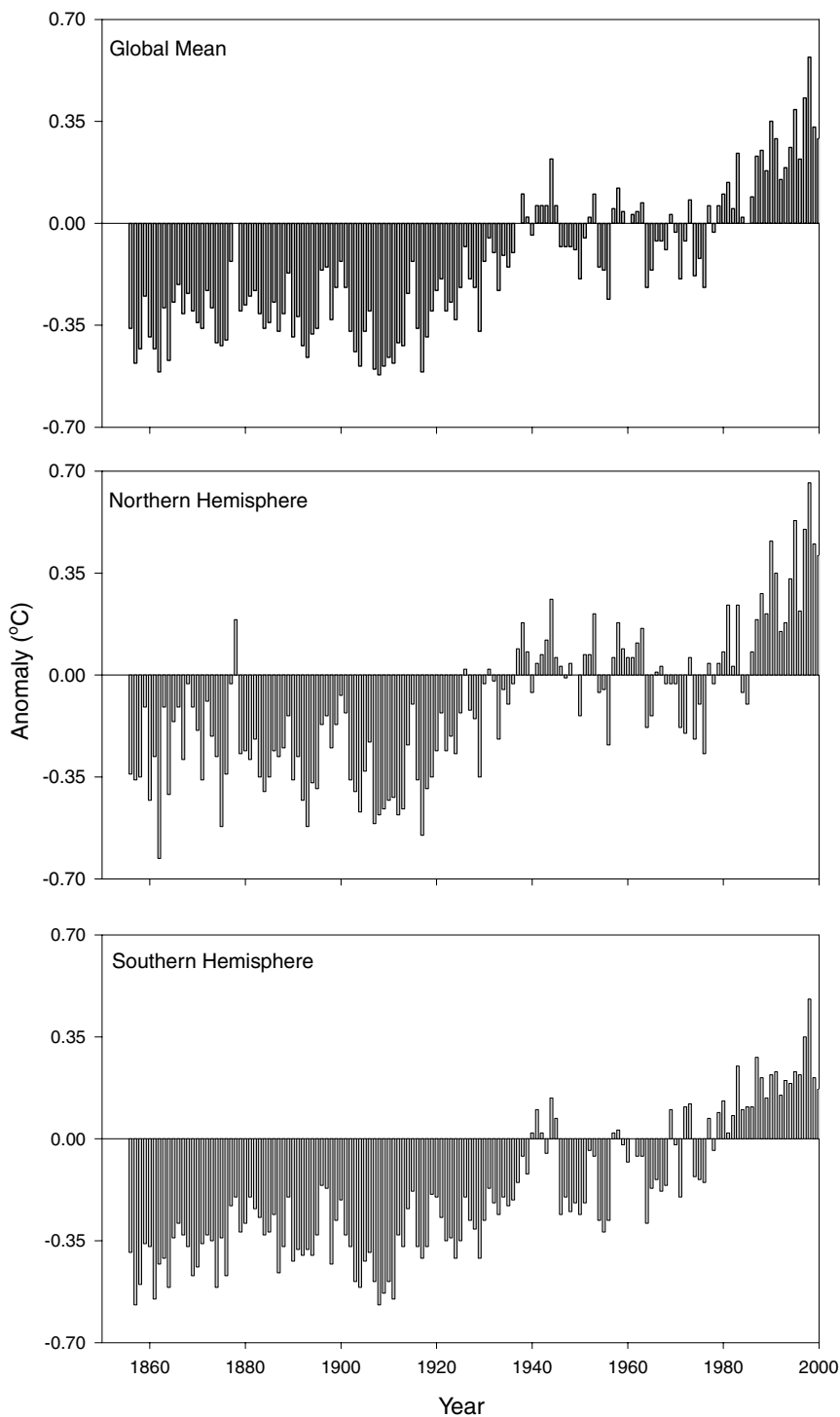


Figure 11.2 Mean annual temperature anomalies for the whole Earth and for the Northern and Southern Hemispheres for the period 1856–2000. The units on the y-axis are the departure from the average for the period 1961–1990. (From Carbon Dioxide Information Analysis Center, 2004.)

Other evidence suggests that global climate change processes may increase nighttime temperatures more than daytime temperatures and that the temperature changes will be larger at mid and high latitudes as compared to the equatorial regions. Still, the observations on temperature are within the natural variability of the climate and there is further disagreement on whether the trends of the past two decades will persist. There have been times when the climate has been both warmer and cooler than present conditions without any influence from humans. By the guidelines of the scientific method, discussed in Chapter 1, we may not be able to conclude that anthropogenic global warming is real yet. This fact has been used by some to justify a lack of action aimed at reducing the atmospheric loadings of greenhouse gases. It is also difficult to appreciate the potential change in our climate due to a change of only a few degrees Celsius. To put this into perspective, consider that the climate has warmed only 5°C (9°F) since the last ice age.

There is additional evidence that the troposphere is warming. The fraction of the Earth's surface covered by glaciers and impacted by permafrost has declined. The length of the growing season has increased at mid and high latitudes. Animals and plants adapted to warm climates have shifted their range toward the poles and to areas higher in altitude as the area with conditions favorable for their survival has shifted. The emergence of some insects, flowering of some plants, and nesting activities of some birds, long the hallmark of the arrival of spring, have been shown to occur earlier. Human and animal diseases normally confined to warmer climates may affect larger geographic areas. All these changes are directly related to warmer temperatures.

Unfortunately, climatic changes are likely to occur as the mean global temperature increases. These changes are as yet relatively unpredictable beyond the knowledge that an increased global temperature will influence the driving forces for our weather. Global warming obviously implies an increase in average temperature, but the changes are not as simple as adding a few degrees to the high and low temperature each day. For a given location, there will be more days each year that surpass some critical value (e.g., 38°C or ~100°F) and fewer days that would be considered extremely cold. The high extremes place the greatest burden on our resources as we run air conditioners and assist sick and elderly persons who have difficulty tolerating the heat. Precipitation patterns will also change. The average annual precipitation for a given location may increase or decrease, and the distribution of precipitation during the year may change. Winters may become wetter and summers drier as the atmosphere warms. The changes in precipitation have the potential to create the greatest problems for humans because of the influence on plant growth. Warmer temperatures will increase the amount of water needed by plants. The increases in temperature with decreases in annual or summer precipitation may make it difficult for plants to grow normally or even survive. Related to changes in precipitation are changes in relative humidity. The amount of water stored in the atmosphere will increase as the temperature rises because more evaporation will occur and because air is able to hold more water at higher temperatures. These changes in humidity will be a driving force behind the changes in precipitation patterns.

11.2.2 Greenhouse Gases

It is known that the atmospheric concentrations of the primary greenhouse gases have increased since preindustrial times. The Industrial Revolution began in England about 1760 and then spread to other countries. The primary greenhouse gases include CO₂, methane (CH₄), nitrous oxide (N₂O), O₃, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆) (Table 11.1). Water can also be considered a greenhouse gas because it too absorbs and releases radiation. The first four gases are naturally occurring, although humans have had a profound impact on their atmospheric concentrations. The remaining gases are the products of human activities.

The influence of a given greenhouse gas on the overall anthropogenic greenhouse effect is related the potency of a gas and its atmospheric concentration. The potency refers to how efficient

Table 11.1 Characteristics of the Primary Greenhouse Gases

Greenhouse Gas(es)	Comments	GWP ^a	Atmospheric Lifetime
CO ₂	Natural and anthropogenic sources; fossil fuel use primary anthropogenic source	1	50–200 years
CH ₄	Natural and anthropogenic sources; rice culture and enteric fermentation primary anthropogenic sources	21	12 years
N ₂ O	Natural and anthropogenic sources; N fertilizer use, biomass burning, and fossil fuel combustion primary anthropogenic sources	310	120–150 years
O ₃	Stratospheric O ₃ blocks ultraviolet radiation; acts as a greenhouse gas in the troposphere; produced by reaction with NO ₂ , CH ₄ , and hydrocarbons in the atmosphere	— ^b	Hours to days
CFCs	Used as refrigerants and blowing agents; being phased out because of the stratospheric O ₃ -depleting potential	3,700–5,400	Days to 400 years
HCFCs	Preliminary substitute for CFCs; also being phased out	90–1,650	1–40 years
HFCs	Replacement for CFCs and HCFCs; long atmospheric lifetime	140–12,000	1–265 years
PFCs	Released during Al production; long atmospheric lifetime	6,500–9,200	3,200–55,000 years
SF ₆	Used as a dielectric in electrical transmission and distribution systems and in Mg casting	23,900	3,200 years

^a Global warming potential over a 100-year time period.

^b Complex dependence as a function of altitude.

a gas is at absorbing heat and is expressed as the *global warming potential* (GWP). The GWP is a relative scale that compares the ability of a gas to absorb heat in relationship to CO₂, one of the least potent of the greenhouse gases. Generally, the GWP is the ratio of warming potential (radiative forcing) for 1 unit mass of a greenhouse gas to the same mass of CO₂ over a specified period of time. A 100-year timeframe is used most often as the standard. To compare the contributions of the greenhouse gases to the anthropogenic greenhouse effect, the emissions can be expressed on the basis of the equivalent C input to the atmosphere, generally as *a million metric tons of C equivalent* (MMTCE). The MMTCE for a given gas is calculated as

$$\text{MMTCE} = (\text{gas emissions in Tg/year}) \times (\text{GWP}) \times 12/44 \quad (11.1)$$

where 12/44 represents the fraction of C in CO₂. With this calculation, 1 MMTCE from CO₂ has the same impact on the anthropogenic greenhouse effect as 1 MMTCE from any other greenhouse gas. You may also see units of Tg CO₂ Equivalents, which differ from MMTCE by the factor of 12/44.

Example Problem 11.1

Various units are used in discussing global climate change; units are not always consistent and can be very confusing. There are two issues. One is the use of various prefixes in the SI system to describe the very large quantities of the various gases. The prefixes that are commonly used are peta (P), tera (T), giga (G), and mega (M), which are used to designate 10¹⁵, 10¹², 10⁹, and 10⁶, respectively. If we

were describing grams, as is often done, then $1 \text{ Pg} = 1000 \text{ Tg} = 10^6 \text{ Gg} = 10^9 \text{ Mg}$. However, the prefixes are also used to designate quantities of other units of mass. For example, a million metric tons (as is used for MMTCE) is 1 Tg or 1000 Gg because 10^6 metric tons (where 1 metric ton is 1000 kg or 1 Mg or 10^6 g) is $10^6 \times 10^6 \text{ g} = 10^{12} \text{ g}$.

Demonstrate that $1 \text{ Pg} = 1 \text{ Gt}$.

$$1 \text{ Pg} = 10^{15} \text{ g}$$

$$1 \text{ Gt} = 10^9 \text{ tons} \times \frac{1000 \text{ kg}}{\text{ton}} \times \frac{1000 \text{ g}}{\text{kg}} = 10^{15} \text{ g} = 1 \text{ Pg}$$

The second issue is the use of either C or CO_2 equivalents. To express CO_2 on a C basis we need to multiply by the fraction of the formula weight of CO_2 that is C, or $12/44$. Therefore,

$$\text{Tg CO}_2 \text{ Equivalents} \times 12/44 = \text{MMTCE} \quad (11.2)$$

It is hoped that some standard units will evolve out of the discussions and there will be less confusion in the future.

Although CO_2 is the least potent greenhouse gas, it contributes the most to the greenhouse effect because of its relatively high atmospheric concentration, which is a result of large emissions. Atmospheric emissions of CO_2 in the United States in 2001 were approximately 1580 MMTCE compared to 176 MMTCE for CH_4 , 98 MMTCE for N_2O , and 21 MMTCE for the combination of HFCs, PFCs, and SF_6 and have been on an upward trend since 1990 (Figure 11.3). Emissions of CFCs and HCFCs are decreasing rapidly. These compounds have been found to contribute to the decline of stratospheric O_3 and are being phased out as part of the Montreal protocol, an international treaty that addresses the release of O_3 -depleting substances worldwide (see Chapter 2).

Water vapor is also a very important radiatively active gas, although the concentrations of water vapor in the atmosphere generally do not change as a direct result of human activities. A warmer climate, however, will induce greater evaporation worldwide and the additional water vapor will likely contribute to greater warming.

Another important characteristic of a greenhouse gas is its atmospheric lifetime. The atmospheric lifetime is 50 to 200 years for CO_2 , approximately 12 years for CH_4 , 120 to 150 years for N_2O , and varying times for the remaining greenhouse gases. The atmospheric lifetime is factored into the GWP, but it also suggests how successful efforts to reduce greenhouse gas emissions might

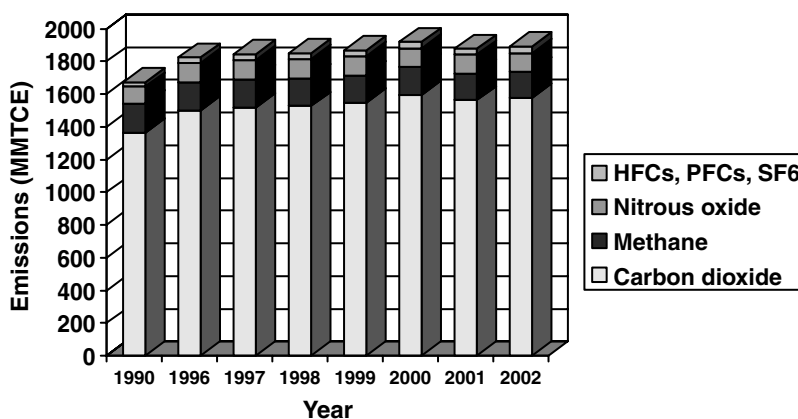


Figure 11.3 Emission trends for greenhouse gases in the United States from 1990 to 2002. (From U.S. EPA, 2004.)

be in the short run. If CO₂ emissions declined dramatically, we would still realize the effects of CO₂ already in the atmosphere for some time, whereas reductions in CH₄ emissions might improve the situation within a few decades. The PFCs and SF₆ are problematic because their atmospheric lifetimes are all in excess of 3200 years.

Coupled atmosphere–ocean general circulation models (AOGCMs) are used to predict the effects of increasing concentrations of greenhouse gases on components of the climate. The models are extremely complex and require considerable computing power to run. The most recent advance in AOGCMs allows a coupling of the atmosphere with the effects of the oceans. Typically, the models will compare the climate considering a 1% increase in atmospheric CO₂ per year. There are many different models in use. For the next century, all are consistent in predicted increases in mean temperatures, ranging from <1°C over some portions of the oceans, 2 to 4°C increase over land at low to middle latitudes, and up to 7°C increase at the polar regions. The greater enhancement of temperature at the polar regions has significant implications for melting of the polar ice caps. Most models also predict increases in the global mean precipitation. However, some regions will experience decreases in annual precipitation or the distribution of precipitation during the year. It is likely that drought will become more common with global climate change. The increases in precipitation may not be sufficient to offset the increased evapotranspirational demands from the increases in temperature. It should be noted, however, that there is still a great deal of uncertainty in the area of climate modeling.

Soils can be a source or a sink for CO₂, CH₄, and N₂O and these gases are discussed in more detail in the following sections. Soils play no role in the cycling of O₃, CFCs, HCFCs, PFCs, or SF₆ and comments on these gases will be very brief. Efforts are already being made to reduce emissions of CFCs and HCFCs. Unfortunately, their replacements are also potent greenhouse gases. Because O₃ is a pollutant in the lower atmosphere, efforts are already under way to reduce O₃ inputs to the atmosphere, and this will have beneficial effects toward reducing global warming.

11.2.2.1 Carbon Dioxide

Carbon dioxide has the highest concentration of all atmospheric greenhouse gases. Because the CO₂ concentration is at least 200 times greater than the other greenhouse gases, it has the highest relative contribution (approximately 60%) to the anthropogenic greenhouse effect. It is the least potent of the greenhouse gases with its contribution to global warming primarily a result of its high atmospheric concentration. The dramatic increase in the atmospheric level of CO₂ since the Industrial Revolution is shown in Figure 11.4. These data are a combination of CO₂ concentrations in samples of air collected at the Mauna Loa Observatory since 1959 and of air bubbles trapped in ice cores. A more thorough appreciation of the reasons CO₂ concentrations are increasing in the atmosphere can be obtained by examining the global C cycle (Figure 11.5). For the time period immediately prior to large-scale human population increases, atmospheric CO₂ concentrations were essentially constant. The primary CO₂ inputs to the atmosphere were CO₂ released from the oceans and from the decomposition of dead plant material. The primary mechanisms for removal of CO₂ from the atmosphere were plant uptake and absorption by the oceans. The inputs were approximately balanced with the outputs and all other C pools were relatively stable. Human activities have taken C stored as recoverable fossil fuels, biomass, and soil organic matter and placed it into the atmosphere as CO₂ at a faster rate than it can be removed by plant growth or by adsorption into the oceans. Atmospheric CO₂ concentrations have increased from approximately 280 parts per million by volume (ppmv) in preindustrial (pre-1750) times to 373 ppmv today. The United States contributes more CO₂ to the atmosphere than any other single nation (Figure 11.6). Nearly all of this CO₂ is from energy usage with some 84% of our energy needs met with energy sources that release C (Figure 11.7).

A summation of the C transfer rates in Figure 11.5 shows that the net transfer of C into the atmosphere is 3 to 5 Gt/year. The 6 to 8 Gt/year placed into the atmosphere from combustion of fossil fuels and deforestation is slightly offset by a net transfer of C into the oceans at 3 Gt/year.

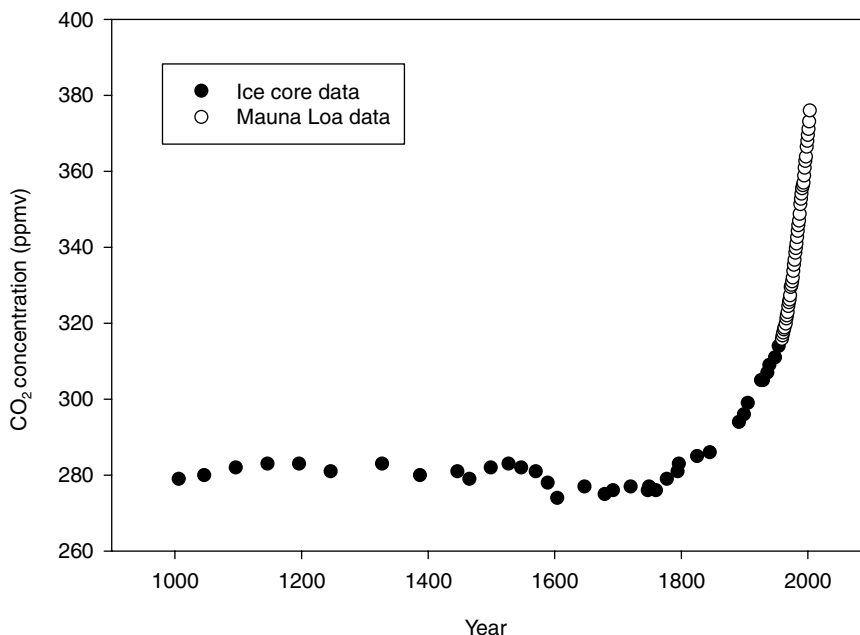


Figure 11.4 Atmospheric CO₂ concentrations from 1006 to 2003 as determined from air trapped in ice and from actual air samples. (From Carbon Dioxide Information Analysis Center, 2004.)

The current mass of C in the atmosphere as CO₂ is approximately 742 Gt with a concentration of 373 ppmv. Considering the ratio of these two values, $373/742 = 0.5$, illustrates that the atmospheric CO₂ concentration increases by approximately 0.5 ppmv for each net Gt of C placed into the atmosphere, or about 1.5 ppmv each year with a net transfer of 3 Gt/year.

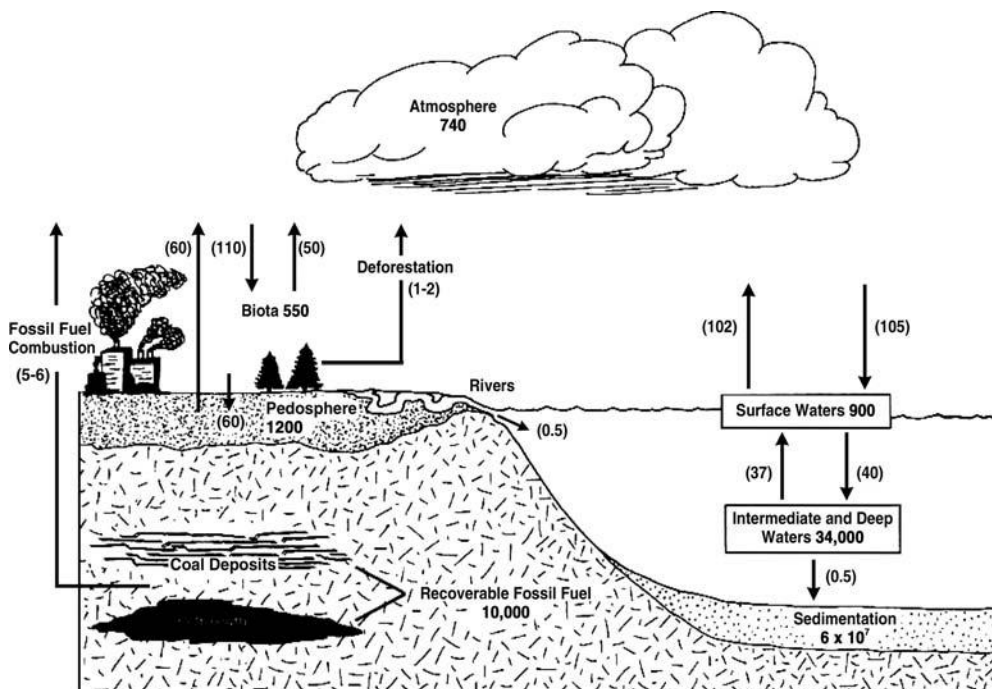


Figure 11.5 The global C cycle (in Gt/year). (From Moore, 1988.)

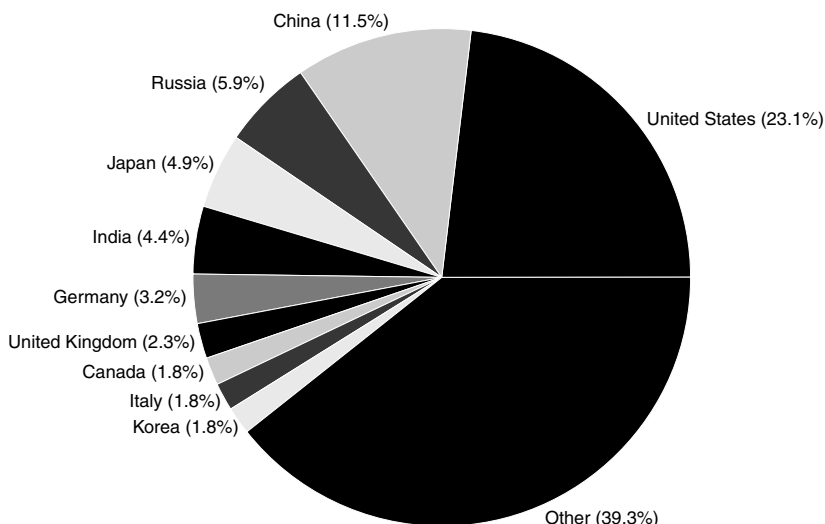


Figure 11.6 The top ten countries for emission of CO₂ from fossil-fuel burning, cement production, and gas flaring for the year 2000. (From Marland et al., 2003.)

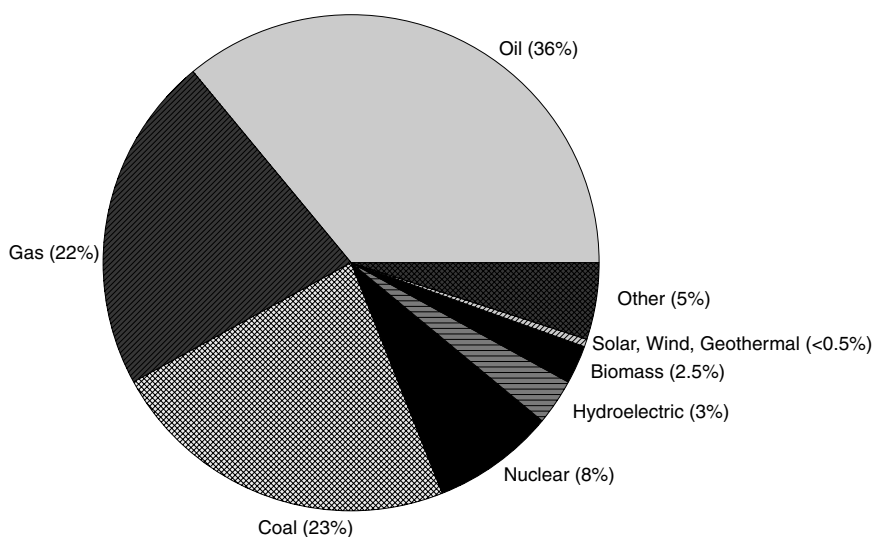


Figure 11.7 Energy use by primary energy source in the United States (Data from U.S. Department of Energy, 2004.)

Humans have some control over several components of the C cycle, including deforestation, combustion of fossil fuels, C lost to the atmosphere because of soil erosion, and, to a lesser extent, the amount of C taken up by growing plants. Carbon used for plant growth is stored both aboveground and in the soil while the plant is alive. Some of the C remains in the soil as organic matter after the plant dies and decomposes. Plants convert atmospheric CO₂ into carbohydrates through photosynthesis and therefore may respond in some fashion to increased atmospheric CO₂ levels. Most plants fall into one of two general categories based on differences in their biochemical pathways for fixing atmospheric CO₂. The *C₃ plants* (e.g., wheat, soybeans, cotton) take CO₂ from the air into mesophyll cells where the Calvin cycle converts it to sucrose. The

C4 plants (e.g., corn, sorghum, millet) also take CO_2 from the air into mesophyll cells, but the fixed CO_2 (as a C_4 molecule) is transported to the bundle sheath cells where the Calvin cycle takes place. This “pumping” of CO_2 from the mesophyll cells into the bundle sheath cells maintains a greater CO_2 concentration gradient between the atmosphere and the mesophyll cells, which increases the ability of the C_4 plants to assimilate CO_2 . Thus, the C_4 plants are more efficient users of CO_2 .

The C_3 plants, as they are less efficient users of CO_2 , will actually increase their photosynthetic rate in response to elevated CO_2 concentrations, provided that other growth factors are not limiting. Thus, we could predict increased growth from C_3 plants as atmospheric CO_2 levels increase. This effect is called CO_2 fertilization. The C_4 plants will also respond positively to increased CO_2 concentrations, although not to the extent of C_3 plants. Both C_3 and C_4 plants tend to use water more efficiently when CO_2 levels are higher. This is because the stomates (openings in leaves that provide the means of gas and water exchange between plants and the atmosphere) do not open as much in the CO_2 -enriched environment, and less water is lost during photosynthesis. This effect is more pronounced with the C_4 plants. In the case of C_3 plants, there is also an increase in plant growth without an increase in water use. In elevated CO_2 environments, both C_3 and C_4 plants can be more efficient in their use of nutrients, especially N, which is a positive response.

Unfortunately, water and nutrients are already the primary limiting factors for plant growth across much of the Earth, and this will likely remain the case as the climate changes. Clearly, if large-scale increases in plant productivity were possible due to increasing atmospheric CO_2 levels, then atmospheric CO_2 concentrations would not be as high as they are today. Increased biomass production has, however, likely reduced the magnitude of the increase in atmospheric CO_2 concentrations. Water may even become more of a limiting factor due to increasing temperatures.

The role of soils in the global cycling of C is quite diverse. First, soil and detritus contain 1200 Gt of C, which is one of the larger pools of C in the global C cycle. The C cycle for cropland ecosystems is outlined in Figure 11.8. Plants fix atmospheric CO_2 during photosynthesis. Plant shoots and roots respire and release CO_2 to the atmosphere. However, as long as the plant is growing new tissue, more C is removed from the atmosphere by photosynthesis than returned by respiration. Soil microorganisms decompose shoots and roots, returning a portion of the C to the atmosphere as CO_2 through respiration, and retaining a portion of the C as soil organic matter. The *humification efficiency* of plants is generally of the order of 10 to 20%. This is to say that 10 to 20% of the C fixed by plants is retained by soil after most of the rapid decomposition of the biomass is complete. Clearly, the significance of soils in C storage should not be overlooked. Worldwide, an estimated 25 billion tons of soil are lost to erosion each year and, assuming 4% organic C content, that represents a potential C input of 1 Gt/year or 20 to 30% of the net increase in atmospheric C each year. Fortunately, not all of that C reaches the atmosphere.

Strategies for dealing with increasing CO_2 levels in the atmosphere fall into two general categories: (1) reducing CO_2 inputs to the atmosphere or (2) increasing the amount of C stored in various C pools. Reducing CO_2 inputs to the atmosphere can be accomplished in a variety of ways. Increasing fuel efficiency will reduce the amount of fossil fuel required to produce the same amount of energy or perform the same amount of work. Generating electricity with nuclear fuel, solar energy, or wind or water power would greatly reduce the amount of coal combustion that is currently required. The use of biomass fuels also falls into the category of reducing CO_2 inputs to the atmosphere even though they produce CO_2 when burned. The difference between biomass fuels and fossil fuels is that biomass fuels recycle CO_2 that was already in the atmosphere, whereas fossil fuels release CO_2 that was removed from the atmosphere a long time ago. In essence, biomass fuels, which are considered renewable resources, reduce the introduction of new CO_2 into the atmosphere by producing energy without utilizing fossil fuels. Slowing deforestation will also reduce CO_2 to the atmosphere as will reducing soil erosion, as discussed above.

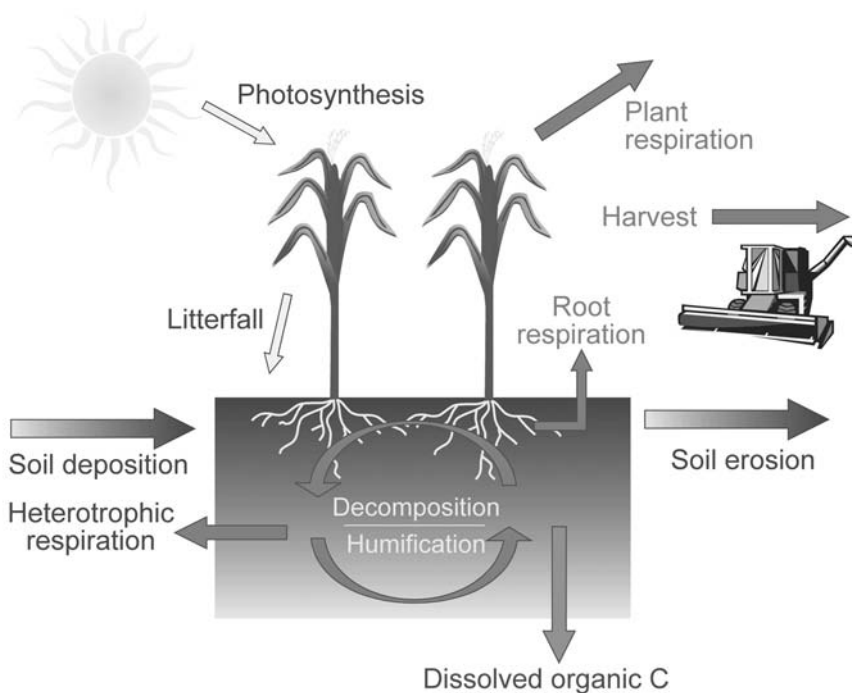


Figure 11.8 Cropland carbon cycle. Overview of the C cycle in cropland ecosystems showing the major fluxes of organic C. (From Council for Agricultural Science and Technology, 2004. With permission.)

Carbon sequestration is a relatively new concept with the aim of increasing the amount of C stored in various pools in the global C cycle. Carbon sequestration can take many forms including placing C in underground geologic repositories, enhancing the amount of C stored in terrestrial ecosystems, and C sequestration in the oceans. In all cases the amount of C stored in pools other than the atmosphere must be increased for the strategy to be effective. The soil is one such pool, but the oceans, geologic formations, and vegetation are other possibilities. Current estimates are that C sequestration could remove 1 Gt C/year from the atmosphere before 2050 if a concerted effort were made to increase vegetation; to reduce C emissions from power plants, automobiles, and other petroleum-consuming processes; and to prevent soil erosion.

When soils are taken out of natural vegetation and used for agricultural production, they will typically lose 25 to 50% of their organic matter, unless properly managed. It is estimated that global soil C losses from agricultural soils have been 50 to 150 Gt over the last several centuries. If we could return that C to soils, this would represent the maximum benefit that could be realized by soil C sequestration. Realistically, it is estimated soil C sequestration could remove up to 40 Gt of C from the atmosphere over the next 50 years. This represents approximately 5% of the C in the atmosphere.

Table 11.2 illustrates potential soil C sequestration in U.S. cultivated soils by various strategies. The climate influences the magnitude of soil C sequestration as well as the suitable strategies. Here, a dry climate refers to areas where potential evapotranspiration exceeds precipitation. This includes an area roughly from the central plains west to the Pacific Ocean. The eastern half of the country would be considered humid. The practices include taking highly erodible land out of production, use of winter cover crops for humid areas, elimination of summer fallow, and adoption of continuous no-till practices.

For the terrestrial ecosystem, revegetation (forests and grasslands), increasing C production on fertile soils, restoration of degraded soils, removal of poor agricultural soils from production, and the promotion of beneficial reuse of organic by-product materials (animal manures, municipal biosolids, etc.) have the potential to increase the amount of sequestered C. Net sequestration by

Table 11.2 Influence of Various Soil C Sequestration Strategies on Potential C Sequestration in Cultivated U.S. Soils (Tg C/year)

Climate Regime ^a	Baseline ^b	Set-Aside of HEL ^c	Winter Cover Crops	Elimination of Summer Fallow	Continuous No-Till	Total
Dry	2.4	3.6	0	1.0	5.4	12.4
Humid	14.7	7.0	22.8	2.2	41.5	88.2
Total	17.1	10.6	22.8	3.2	46.9	100.6

^a Dry denotes potential evapotranspiration exceeds precipitation.

^b Soil C stock in 1997.

^c HEL = highly erodible land not already taken out of production.

Source: Sperow, V. et al., *Climate Change*, 57, 319–339, 2003.

the terrestrial ecosystem is currently at approximately 2 Gt/year, but some scientists believe this could be doubled through reforestation, conservation tillage, and crop residue management. Under ideal conditions, soils can realize a net increase of 500 kg C/ha/year while accumulating C. This rate cannot be sustained indefinitely, however, as eventually soils reach a new equilibrium and no longer accumulate C. The reader is reminded of the magnitude of the amounts of C that need to be considered. Significant changes in the size of any C pool will require some degree of global cooperation, and the most likely outcome will be a decrease in the rate of increase of CO₂ levels in the atmosphere.

Example Problem 11.2

There are approximately 128 million ha of cultivated land in the United States. If all of this land could sequester 500 kg C/ha for 1 year, what fraction or percentage of the net loading of 3 Gt C/year into the atmosphere would this represent?

$$128 \times 10^6 \text{ ha} \times \frac{500 \text{ kg C}}{\text{ha}} \times \frac{1 \text{ ton}}{1000 \text{ kg}} \times \frac{1 \text{ Gt}}{10^9 \text{ ton}} = 0.064 \text{ Gt}$$

$$\frac{0.064 \text{ Gt}}{3 \text{ Gt}} \times 100 = 2.1\%$$

The remaining C sequestration approaches are more experimental at this time. Improved technologies for capturing CO₂ need to be developed and the concept of injecting captured CO₂ into the oceans or geologic formations should continue to be evaluated. Carbon dioxide injection is already practiced in oil-extraction operations, but issues related to the total assimilation capacity and the length of time the CO₂ would remain trapped require further attention.

Overall, the easiest actions to implement are the “no regret” type of actions. These reflect changes that should be made regardless of the global warming problem. There are a number of reasons, for example, that soil erosion should be prevented or that fuel efficiencies should be improved. If global warming turns out to be less serious than some currently believe, the resources spent on those actions would not be wasted.

11.2.2.2 Methane

Methane is produced by *methanogenic bacteria* any time C-based substances are decomposed anaerobically. These conditions are typically found in flooded soils, in the digestive systems of

ruminant animals, and when organic by-products are stored or handled as liquids, as is often done with animal manures and municipal biosolids. Humans have increased CH_4 concentrations in the atmosphere by increasing the amount of C that is metabolized anaerobically. Similar to CO_2 , atmospheric CH_4 concentrations were relatively constant prior to large-scale human population of the Earth. Wetlands and native ruminant animals were the primary sources of CH_4 at that time. Today, rice culture, domestic ruminant animals, landfills, and our own use of CH_4 as a fuel source provide additional CH_4 to the atmosphere (Figure 11.9). Atmospheric CH_4 concentrations have increased from approximately 790 parts per billion by volume (ppbv) in preindustrial times to 1800

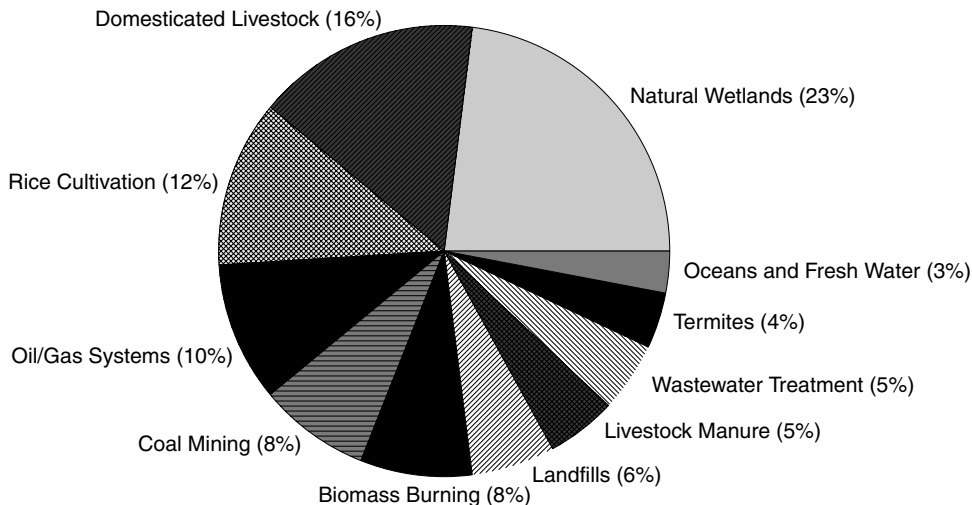


Figure 11.9 Sources of atmospheric methane emissions. (From U.S. Environmental Protection Agency, 1999b.)

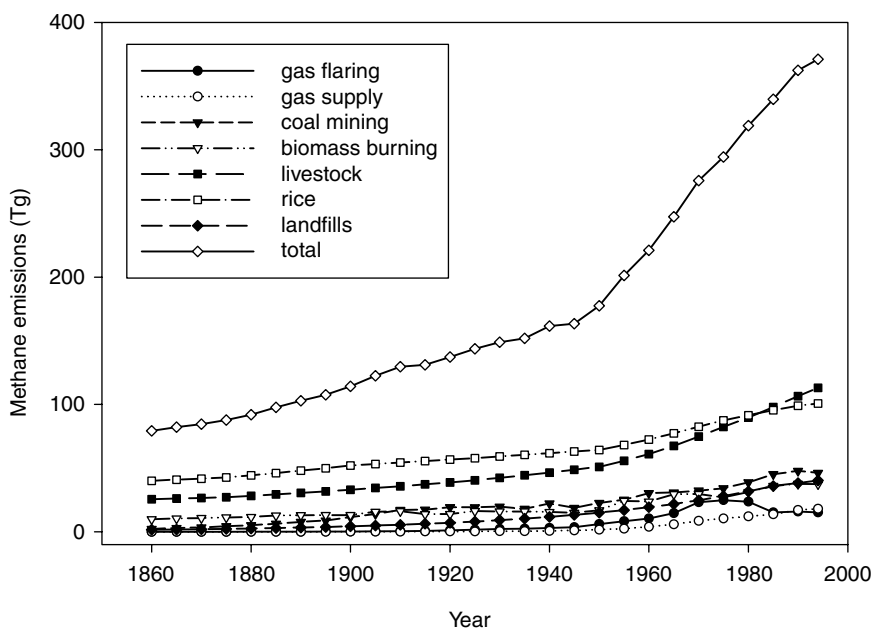


Figure 11.10 Global methane emissions from 1860 to 1994. (From Stern and Kaufmann, 1998.)

ppbv (or 1.8 ppmv) today. Figure 11.10 provides a breakdown of global annual emissions of CH_4 with time and by source. Of all the greenhouse gases, CH_4 emissions are the most closely tied to the production of food on a global basis. It is estimated that one third of global CH_4 emissions is from rice culture and from the digestive processes and by-product handling associated with domesticated livestock alone.

Methane is a more potent greenhouse gas than CO_2 . With an atmospheric concentration of approximately 1800 ppbv, CH_4 contributes 15% to the anthropogenic greenhouse effect. The unique thing about CH_4 is the short atmospheric lifetime of 12 years compared with CO_2 , N_2O , or CFCs (Table 11.1). The fate of atmospheric CH_4 is not completely understood. It is known that soil bacteria responsible for nitrification can oxidize CH_4 as well as NH_4^+ . Therefore, aerated low-N soils can be a CH_4 sink. However, most CH_4 is dissipated via reaction with tropospheric hydroxy (OH). The short atmospheric lifetime of CH_4 also suggests that efforts to reduce CH_4 emissions could be effective in slowing the increase in the rate of global warming.

Efforts to directly reduce CH_4 emissions resulting from food production will not be easily implemented because of increasing population and demand for food in areas of the world where rice is a major staple. Rice production in the United States utilizes <1.5% of our cultivated land area, and CH_4 emissions from these lands are insignificant on a global scale. Research may help reduce the amount of CH_4 produced per unit of rice produced. This could be accomplished by breeding rice with a higher grain-to-straw ratio, which results in less straw available for anaerobic decomposition, or by increasing the proportion of upland rice varieties grown. Other water-use strategies may reduce CH_4 emissions from rice production.

Research may also reduce CH_4 emissions from livestock, particularly ruminants. The CH_4 emitted from these animals reflects a loss of feed energy and is inefficient. Efforts to increase feed efficiency or to increase the rate of weight gain by livestock will decrease the amount of CH_4 emitted. Large sectors of the world population have low-quality diets and, historically, diet improvement has come about by increasing the proportion of meat in the diet. This would suggest increasing the numbers of domestic animals in some areas of the world.

Direct efforts at reducing CH_4 emissions will need to focus on natural gas distribution systems, fossil fuel production methods, and landfills and other by-product-handling methods. It has been estimated that some natural gas distribution systems lose as much as 3% of the gas through leakage. Oil exploration, coal mining, and coalbed method production also release large amounts of CH_4 as do landfills and some organic by-product-handling systems. In each of these examples there are preventable losses of CH_4 , and methods developed for capturing or retaining CH_4 will benefit the global climate problem.

11.2.2.3 Nitrous Oxide

Nitrous oxide contributes approximately 5% to the greenhouse effect. Concentrations have increased in the past 200 years from approximately 270 to 317 ppbv. Nitrous oxide is produced in soils through both biotic and abiotic processes. Various microbial pathways produce N_2O , including nitrification and denitrification. Nitrous oxide is released from all soils, regardless of cultivation or fertilization, although N fertilization will increase N_2O emissions because of the greater amount of substrate available for nitrification and denitrification. Emissions of N_2O from soils can be stimulated by land use conversion, particularly the conversion of land from any native vegetation to agricultural production. As discussed previously, soil organic matter levels tend to decrease when soils are first cultivated. Some of the N in the organic matter will be lost as N_2O . Nitrous oxide is also produced when reduced-N compounds in fossil fuels or other biomass materials are oxidized during combustion. As a result of increases in the activities described above, the concentration of N_2O in the atmosphere has increased compared with preindustrial times. Figure 11.11 provides a summary of atmospheric N_2O sources for the United States.

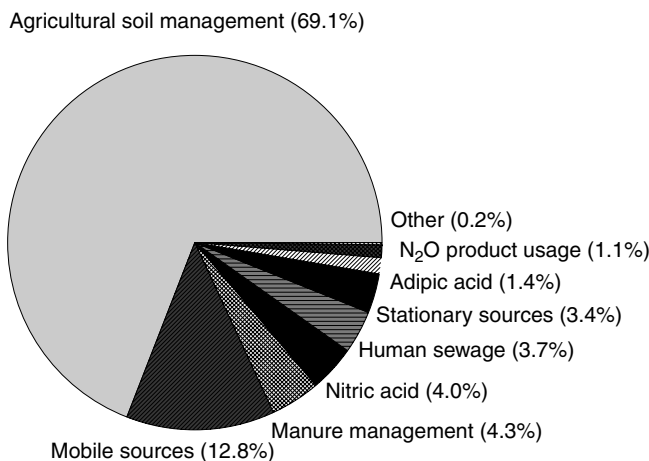


Figure 11.11 Nitrous oxide emissions from the U.S. in 2002. (From U.S. EPA, 2004.)

Nitrous oxide is a more potent greenhouse gas than CO_2 or CH_4 , although it contributes only 5% to the anthropogenic greenhouse effect. Previously described means for reducing CO_2 emissions, such as reducing fossil fuel use and conserving soil organic matter, will also reduce N_2O emissions because N is an integral component of fossil fuels, biomass, and soil organic matter. Direct efforts toward reducing N_2O emissions will have to address fertilizer N use. Fertilizer-derived N_2O emission is a complicated process that can be influenced by factors such as fertilizer type, N rate, application method, tillage, soil moisture, temperature, soil organic matter content, and microbial activity (see Chapters 5 and 8). Overall, a reduction in fertilizer-derived N_2O emissions will require increases in N use efficiency, which will occur to some extent with elevated atmospheric CO_2 levels. Methods for increasing N use efficiency are discussed in Chapters 5 and 8. At present, fertilizer-derived N_2O emissions are estimated to account for 2.5% of global N_2O emissions, assuming that approximately 1.0% of fertilizer N is lost as N_2O . Nitrous oxide emissions due to fertilizer use would be expected to increase worldwide since N fertilizer use is increasing, particularly in countries with high population densities and increasing food demands.

The soil C sequestration strategy may involve increased use of N fertilizers to stimulate biomass production on cropland. This comes at a cost in terms of increased CO_2 emissions from the production and use of the fertilizers themselves, and increased N_2O emissions from the N fertilizers. A high N-fertilizer use efficiency will provide the maximum biomass production per unit of N applied. Thus, increased N-fertilizer use efficiency is an essential component of many strategies to reduce greenhouse gas emissions.

11.2.3 Uncertainties and Complexities

Within the general topic of climate change, the unknown far outweighs the known. Beginning with the climate itself, it is generally accepted that the climate will change, although the nature of the changes is largely unpredictable. One of the reasons for the uncertainty is the large number of feedback mechanisms. That is, a change in one thing will induce additional changes in other parameters such that the net effect of the first change becomes difficult to predict. A simple example was given earlier when it was noted that we know that the greenhouse gases are radiatively active and warm the atmosphere. However, it cannot be said with certainty that continued increases in the concentrations of the gases will cause a continued proportional increase in warming. It is useful to discuss these feedbacks because they influence some of the proposed actions for responding to

global climate change. Evaluating uncertainties also assists in appreciating the complexity of the global warming problem. Bear in mind that feedbacks can be both positive and negative. Several examples are offered to illustrate this complexity.

Undoubtedly water vapor will play a role in potential climate changes. As the climate warms, there will be greater evaporation because more sensible heat is available and warmer air can hold more water than cooler air. The higher concentration of water vapor in the atmosphere may produce more cloud cover. If that cloud cover occurs frequently as a uniform layer (stratus type) at low altitudes over large areas, the clouds may have a net cooling effect because they reflect shortwave radiation back into space (see Figure 11.1). If the cloud cover occurs frequently as a broken layer (cumulus type), the additional water vapor will likely absorb heat and contribute to warming. The additional water vapor will also increase the OH radical concentration in the troposphere. Hydroxyl radicals can react with both CH_4 and O_3 , reducing their concentrations, and acting as a positive feedback for atmospheric warming.

The increasing temperature will have a multitude of effects. Warmer soils will induce oxidation of C and the total amount of C stored in soils may decrease, resulting in a further increase in atmospheric CO_2 concentrations. This is particularly a concern in polar regions where large amounts of C are stored in soils that are currently frozen most or all of the year. As stated earlier, temperature increases are predicted to be the greatest at high latitudes. Warmer air temperatures may also allow the northward expansion of forested regions. Provided that the reforestation is not accompanied by an equivalent amount of deforestation elsewhere, this could increase CO_2 sequestration. Warmer oceans may support higher phytoplankton populations, which absorb CO_2 , but warmer water holds less CO_2 itself. Adsorption of heat by the oceans makes less heat available for warming the atmosphere, but could have adverse effects on marine ecosystems.

One aspect of global climate change that is often forgotten is the potential adaptability of the population to the changing climate. The changes are sometimes considered in a catastrophic context — productive lands suddenly transformed to desertlike areas. Climate change will occur gradually, and the population and food production practices will have to adapt. The growing of grain crops may need to take place at higher latitudes in the Northern Hemisphere. Canada and northern areas of the former Soviet Union and China could become more important grain-producing areas than they are today. The shift in production would occur gradually over a number of years or even decades. In addition, crop breeding and biotechnology may produce crops that are more heat and drought resistant. These points are not intended to minimize the significant economic and social issues associated with a shifting agriculture, but rather to illustrate that adaptations are possible.

As the net effects of the increase in anthropogenic greenhouse gas concentrations in the atmosphere are impossible to predict at this time, so are the net effects of any actions taken to reduce the emissions of any of the gases into the atmosphere. Most experts would agree that significant climatic changes have already been induced, although we do not yet know what they are. It is fairly certain that the climate has warmed or will warm as a whole and that the resulting net effects will not likely be favorable. Therefore, any realistic efforts made to reduce emissions of greenhouse gases would seem worthwhile regardless of the uncertainties.

In December 1997, many countries in the world participated in the Kyoto Conference, held in Kyoto, Japan, in an attempt to reach global consensus on a strategy for reducing greenhouse gas emissions. The resulting *Kyoto Protocol* states that global emissions of greenhouse gases will be reduced to an average of 5.2% below 1990 emission levels by the period 2008 to 2012. The United States agreed to 7% below 1990 levels, the European Union to 8%, and Japan to 6%, while other countries have less stringent requirements. The gases covered include CO_2 , CH_4 , N_2O , HFCs, PFCs, and SF_6 . The agreement also allows credit for C sinks, although the mechanism for doing so has not been worked out. This global effort is encouraging, but as of this writing the United States has not formally ratified the agreement and it is unlikely the objectives will be met.

11.3 ACIDIC DEPOSITION

Although acidic deposition has been recognized as a problem for more than a century, recent studies suggest there is still much to be learned, as noted in the 1998 *National Science and Technology Council* (NSTC) and 2000 *National Atmospheric Deposition Program* (NADP) reports. As one of the most significant, highly publicized, and controversial aspects of atmospheric pollution, acidic deposition has been a major atmospheric research focus for the last 40 years. A principal reason for the increased interest has been the involvement of human emotions combined with media sensationalism that has enhanced public concern about environmental issues (see Chapter 1 for further information). For example, many envision acid rain as the result of horrendous industrial pollution that literally rains down upon the Earth resulting in serious and irreversible environmental damage. Technically, however, the term *acidic deposition* — which includes not only rainfall, but also acidic fogs, mists, snowmelt, gases, and dry particulate matter — is a more precise description of the acid rain problem. The primary origin of acidic deposition is the emission of sulfur dioxide (SO_2 ; Chapter 7) and N oxides (NO_x ; Chapter 5) when fossil fuels are burned for energy production (see Figure 11.12). Other important components of atmospheric emissions include mercury (Hg), volatile organic compounds (VOCs), and particulate matter, which are only mentioned briefly in this chapter.

Adverse *human and animal health effects* have been correlated with high acidic aerosol exposures according to the U.S. EPA (2001). Air quality can be reduced due to increased S-containing particulate matter that can be deposited as dry particles or dissolved to produce acidic substances.

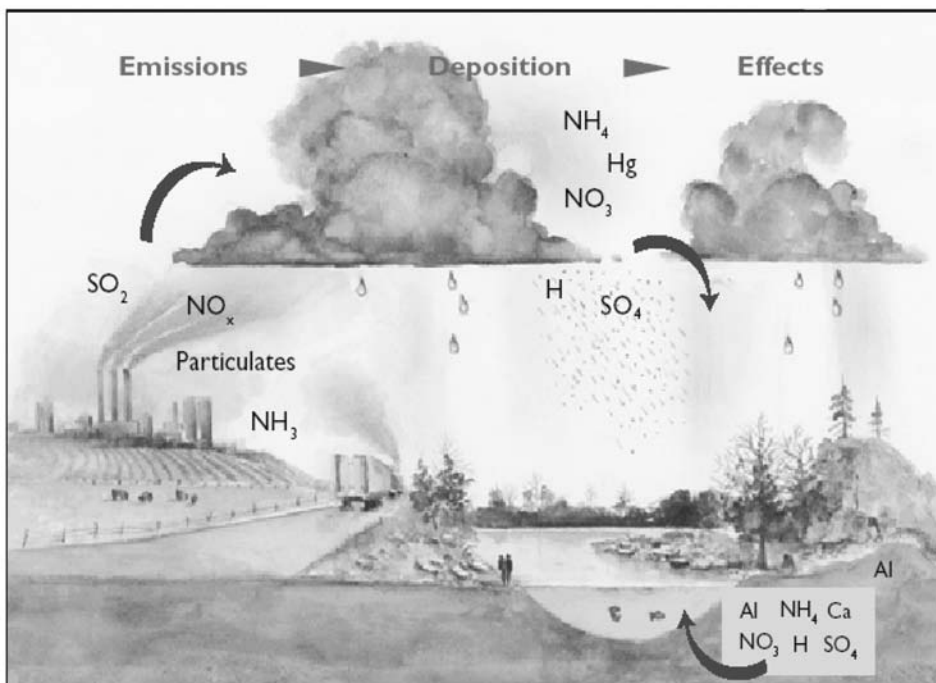


Figure 11.12 (Color figure follows p. 242.) Acid deposition. Acidic deposition is a complex problem that has primarily originated from burning of fossil fuels. Although it was regarded as a simple problem that was limited in scope when first identified some 40 years ago, scientists now know that acids and acidifying compounds can move through terrestrial, biological, and surface water environments, resulting in a series of adverse ecological effects. (From Driscoll, C. T. et al. 2001. Acid rain revisited: advances in scientific understanding since the passage of the 1970 and 1990 Clean Air Act Amendments, Hubbard Brook Research Foundation, *Sci. Links Publ.*, 1, 1, 2001. Available at http://www.hubbardbrook.org/hbrf/publications/Acid_Rain_Revisited.pdf. With permission.)

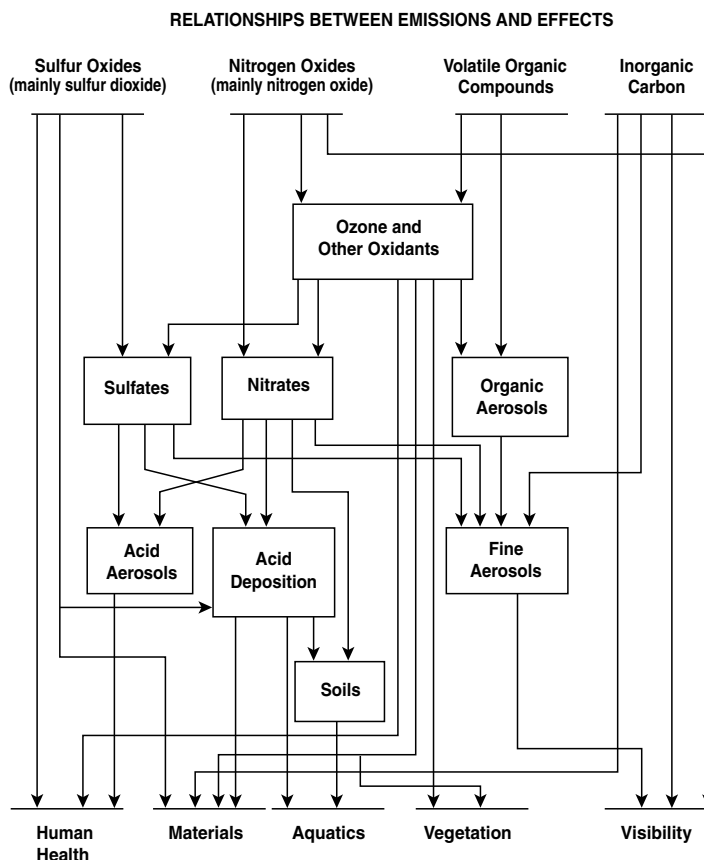


Figure 11.13 Relationships among acidic deposition-related emissions, products, pathways, and human and environmental effects. (From NAPAP Report to Congress, 1992.)

Acidic deposition can also affect structures such as buildings, sculptures, and monuments that are constructed of weatherable materials that consist of limestone, marble, bronze, copper (Cu), and galvanized steel. Although acid soil conditions are known to influence the growth of plants, agricultural impacts related to acidic deposition are less of a concern because of the buffering capacity of most of these ecosystems (NSTC, 1998). When acidic substances are deposited in lakes, streams, forests, and other natural ecosystems, either by wet or dry deposition, a number of adverse environmental effects are believed to occur. Among the most serious are direct impacts to vegetation, particularly forests, and changes in soil and surface water chemistry that can adversely affect plant, animal, and aquatic life (Vance, 2002). The relationships among acidic deposition-related emissions and the products, pathways, and effects on human health, materials, and different environments are shown in Figure 11.13.

In this section we examine political policies and treaties, address the sources and geographic distribution of acidic deposition, describe the more common types of human, material, and ecosystem problems caused by acidic deposition, and give an overview of some remediation efforts currently used to reverse the effects of acidification.

11.3.1 Legislative Acts and Programs

The issue of acidic deposition crosses state and national boundaries because, although acidic compounds can be deposited short distances from the source of pollution, they may also be transported hundreds of kilometers before returning to the Earth in rainfall or other forms of wet

and dry deposition. It has been estimated, for example, that 30 to 40% of the S deposited in the northeastern U.S. originated in the industrial Midwest. On an international scale, the United States and Canada have debated the sources of acidic deposition and the economics of reversing acidification in eastern North America for years and have only recently developed a strategy to address the problem. Similarly, in Europe, the small size of many countries means that emissions in one industrialized area can readily affect forests, lakes, and cities in another nation. A study estimated that 17% of the acidic deposition falling on Norway originated in Britain and that 20% of the acidic deposition in Sweden came from Eastern Europe. Political changes and ongoing economic instability in Eastern European countries that burn high-S coal for energy generation often slowed the implementation of international agreements to reduce emissions of acid-producing compounds.

Most industrialized countries concluded that the acidic deposition issue is serious enough to proceed without final resolution of all scientific issues, a process that could take decades. For example, 21 European nations signed a "Long-Range Transboundary Air Pollution" agreement that targeted reductions in SO₂ emissions. Progress has been slow because of the lack of alternative energy sources to those that produce SO₂ and NO_x and the billions of dollars needed to further reduce emissions of these gases from current sources. Unfortunately, as with many other environmental issues, solutions to the acidic deposition problem are complex, expensive, and long term in nature. In addition, a major cause of a significant level of uncertainty associated with acidic deposition is the fact that other changes in atmospheric chemistry and global climate change have paralleled the increase in acidic deposition. One approach that has reduced SO₂ emissions has been the use of low-S coals by power plants. This has benefited Wyoming's economy because more than 40% of the nation's coal comes from this state. Large coal deposits that are low in S and close to the Earth's surface have made Wyoming coal a major energy resource for numerous states and countries with coal-burning power plants.

In the 1960s and 1970s, both European and North American scientists identified large-scale, regional problems associated with acid-producing sources that resulted in severe impacts to the environment. In North America, the *metal-smelting operations* in Sudbury, Canada were identified as a principal source of SO₂ and other atmospheric pollutants that killed local vegetation and influenced air quality for great distances downwind of the polluting sources (see the Environmental Quality Issues/Events Box: Restoration of Sudbury, Canada, p. 447). Canada and the United States developed federal programs to study the effects of acid deposition in the mid-1970s; the *Canadian Network for Sampling Precipitation* was initiated in 1976 and the *U.S. National Atmospheric Deposition Program* began in 1978.

The 10 years of coordinated research activities under the EPA *National Acid Precipitation Assessment Program* (NAPAP) during the 1980s, involving hundreds of prominent international scientists, led to the publication of numerous reports related to "Acidic Deposition: State of the Science and Technology" that were mandated by the *Acid Precipitation Act* of 1980. Later, in 1992, an NAPAP Report to Congress was developed in accordance with the Acid Rain Program under Title IV (Acid Deposition Control) of the 1990 Amendment to the 1970 *Clean Air Act*, which summarized the findings of the NAPAP and presented the expected benefits of the *Acid Deposition Control Program* (NAPAP, 1992). Proposed mandates included an annual 9.1 million Mg reduction in point-source SO₂ emissions below 1980 levels and a national limit of about 13.6 million Mg (8.5 million Mg from electric utilities and 5.1 million Mg from point-source industrial emissions), which is an approximate 40% decrease from 1980 levels. A reduction in NO_x of about 1.8 million Mg from 1980 levels has also been set as a goal; however, while NO_x levels have been fairly constant since 1980, projections estimate a potential rise in NO_x emissions, primarily from gasoline emissions. In 1980, the U.S. levels of SO₂ and NO_x emissions were 23.5 and 22.6 million Mg, respectively.

Atmospheric deposition of Hg has recently received considerable attention. Since the mid-1990s, the *National Atmospheric Deposition Program Mercury Deposition Network* (MDN) has sampled wet deposition samples from surface waters, forested watersheds, and other ecosystems

from numerous sites in the United States and Canada. In addition, fish have also been analyzed for Hg. Samples of wet deposition and fish are analyzed for total Hg and methylmercury, a potentially toxic form of Hg. Thus far, 43 states and eight Canadian provinces have issued health advisories warning the public against consuming fish from waters that have tested high in fish tissue Hg concentrations.

11.3.2 Sources and Distribution

Typical *sources of acidic deposition* include coal- and oil-burning electric power plants, automobiles and other vehicles, and large industrial operations (e.g., smelters) (Figure 11.14). Once S and N gases enter the Earth's atmosphere they react very rapidly with moisture in the air to form sulfuric (H_2SO_4) and nitric (HNO_3) acids, respectively. The pH of *natural rainfall* in equilibrium with atmospheric CO_2 is about 5.6; however, as shown in Figure 11.15c for the United States, the average pH of rainfall is less than 4.3 in some areas. The *nature of acidic deposition*, e.g., the relative percentages of H_2SO_4 and HNO_3 present, is controlled largely by the geographic distribution of the sources of SO_2 and NO_x . In the United States, H_2SO_4 is the main source of acidity in precipitation in the Midwest and Northeast because coal-burning electric utilities in these areas and Canada also emit large quantities of SO_2 . In the western United States, utilities and industry burn coal with a lower S content; HNO_3 may be of greater concern, particularly in densely populated areas such as California where cars and other vehicles that burn gasoline are major sources of NO_x . The geographic nature of SO_2 and NO_x emissions and the acidity of precipitation in the United States are clearly shown in Figure 11.15.

Unquestionably, emissions of SO_2 and NO_x have increased since the beginning of the 20th century (Table 11.3), due to *accelerated industrialization* in developed countries and *antiquated processing practices* used in the early 20th century that still function in some undeveloped countries. However, after a decade of research during the 1980s, the EPA NAPAP concluded there were some definite impacts due to acidic deposition that warranted remediation. One major consequence of efforts to improve air quality in both the United States and Europe has been the reduction in SO_2 emissions since the mid-1990s. Evidence in northeastern United States has

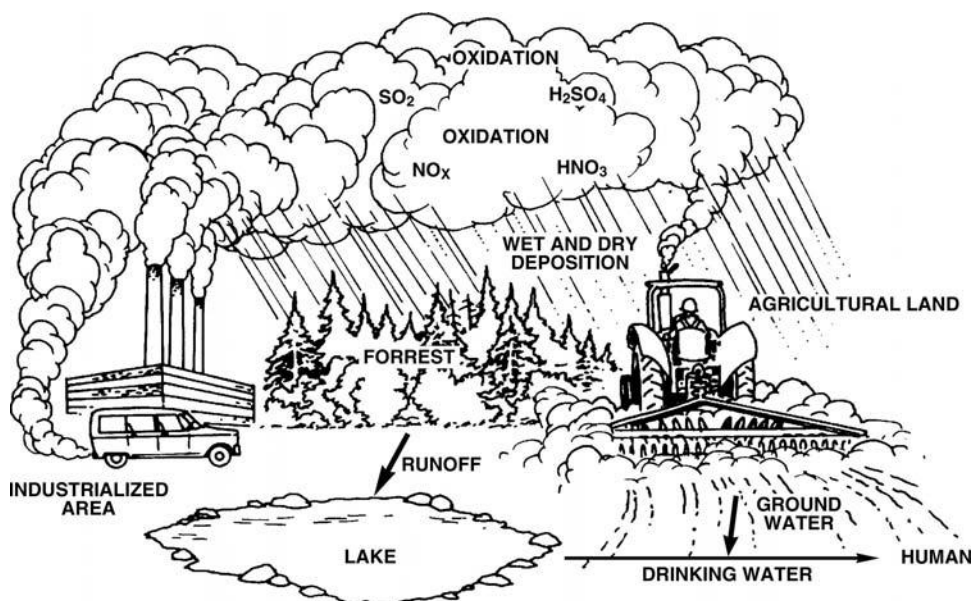


Figure 11.14 Generalized process of the production and distribution of acidic deposition from source to different ecosystems. (Adapted from U.S. Environmental Protection Agency, 1980.)

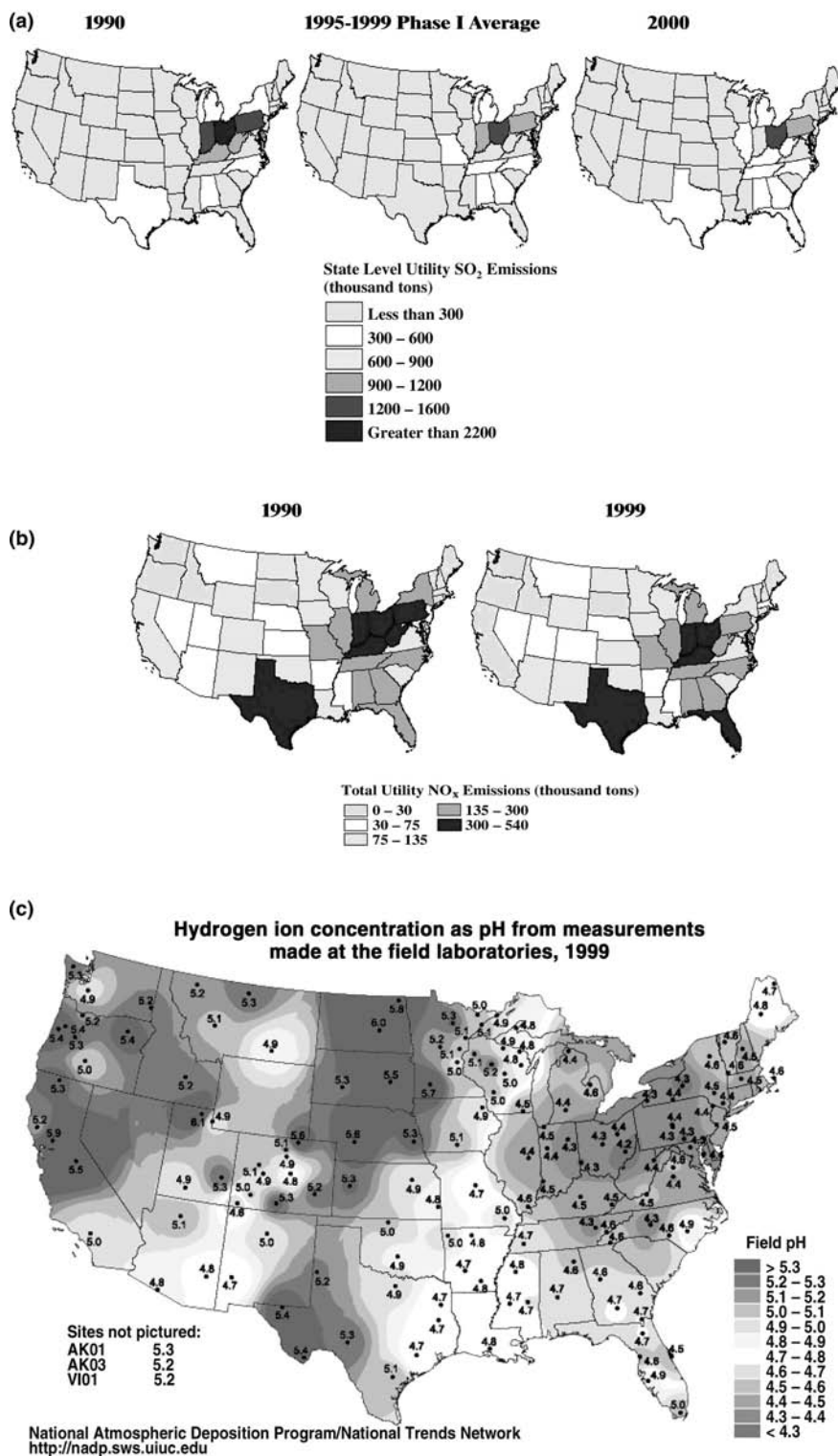


Figure 11.15 Geographic distribution of (a) 1990 and 2000 SO₂ emissions; (b) 1990 and 1999 NO_x emissions; and (c) acidity (H⁺ concentration) of United States precipitation in 1999. (Adapted from the EPA Clean Air Market Programs and the National Atmospheric Deposition Program Trends Network Web sites.)

Table 11.3 Historical U.S. Trends in the Emissions of Nitrogen and Sulfur Oxides (million Mg/year)

Year	Nitrogen Oxides	Sulfur Dioxides
1900	2.37	9.06
1910	3.72	15.7
1920	4.68	19.2
1930	7.27	19.1
1940	6.69	18.1
1950	9.16	20.3
1960	12.8	20.2
1970	19.6	28.3
1975	21.0	25.4
1980	22.1	23.5
1985	21.3	21.5
1990	21.9	21.5
1991	21.1	20.9
1992	22.4	20.7
1993	22.8	20.4
1994	23.1	19.8
1995	22.7	17.4
1996	23.6	17.6
1997	23.9	18.1
1998	23.6	18.2
1999	23.1	17.5
2000	22.6	16.5

Sources: U.S. EPA National Air Quality and Emissions Trends 1996 Report (U.S. EPA, 1996) and 2003 Report at <http://www.epa.gov/air/airtrends/aqtrnd03/appenda.pdf>.

verified these reductions; however, NO_x emissions and NO_3^- levels in rain waters have remained consistent since the 1980s. Although SO_2 has been reduced primarily from restrictions placed on energy power plant emissions, slow recovery of the ecosystems affected over time by acidic deposition is still a concern. See Chapter 7 for more information on S.

Example Problem 11.3

Uncontaminated rainwater should have a pH around 5.6. According to the pH scale, water with equal amounts of H^+ and OH^- has a pH level of approximately 7. The reason rainwater pH is lower than 7 is due to CO_2 chemistry and the formation of carbonic acid (H_2CO_3). The acidity of uncontaminated rainwater (pH 5.6) is

$$\text{pH} = 5.6 = -\log (2.5 \times 10^{-6} \text{ M H}^+)$$

or 0.0000025 mol of H^+ per liter of water.

An acid rain with a pH of 4 would contain

$$\text{pH} = 4.0 = -\log (1 \times 10^{-4} \text{ M H}^+)$$

or 0.0001 mol of H^+ per liter of water, which is a 40-fold increase in H^+ concentration compared to uncontaminated pH 5.6 rainwater.

11.3.3 Human Health Effects

Both *direct and indirect effects on human health* have been attributed to acidic deposition. Direct human health problems are the result of long-term exposure to acidic deposition co-pollutants such as O_3 , NO_2 , and small particulate matter (PM_{10} or $PM_{2.5}$ — particles less than 10 or 2.5 μm , respectively) (see Figure 11.13). These materials are respiratory irritants that cause pulmonary edema, which increases fluids in the lungs that can lead to death in severe cases. Individuals with *respiratory ailments* such as asthma, emphysema, or bronchitis are more sensitive to low-level O_3 exposures; symptoms can include headaches, dry cough, or irritation of the mucous membrane, as well as eye and nose irritation. Sulfur dioxide at high levels is also a known respiratory irritant, but is generally absorbed high in the respiratory tract so that it does not affect the lungs or sensitive alveoli. Particulate matter in the atmosphere can accentuate respiratory problems as was noted in the United Kingdom when coal was the dominant fuel source for domestic heating. This phenomenon, termed *London Fog*, was suspected to be the cause of an increase in the average death rate during a severe week of pollution in 1952.

Indirect human health effects due to acidic deposition are often more significant than are direct effects. Some of these concerns center around *contaminated drinking water supplies* and *consumption of fish* that contain potential toxic metal levels. With increasing acidity (e.g., lower pH levels), metals such as Al, Cu, Hg, cadmium (Cd), lead (Pb), and zinc (Zn) become more bioavailable. However, acidic deposition impacts to drinking water supplies have been limited and are associated primarily with cisterns and some surface water sources. The greatest human health impact may be the consumption of fish exposed to elevated Hg levels that bioaccumulate in the food chain. Freshwater pike and trout have been identified as the fish species that contain the highest average concentrations of Hg. The most susceptible individuals to impacts from acidic deposition and its precursor substances would be those who live in an industrial area, have respiratory problems, drink water from a cistern, and consume a significant amount of freshwater fish in their diet.

As mentioned above, a long-term urban concern is the possible impact of acidic deposition on *municipal water systems* that rely on surface waters to provide drinking water, such as in the Catskills of New York. Many municipalities make extensive use of Pb and Cu piping in water-distribution systems. For example, questions have recently been raised about human health effects related to the slow dissolution of some metals (Cu, Pb, Zn) from older plumbing materials when exposed to more acidic waters.

11.3.4 Material and Cultural Resource Impacts

Different types of materials and cultural resources can be affected by air pollutants that are either the precursor constituents or actual products of acidic deposition (Table 11.4). While the effective *corrosion rates* for most metals have decreased since the 1930s, data from three U.S. sites indicate wet and dry acidic deposition may account for 31 to 78% of the dissolution of Cu and galvanized steel structures. In urban or industrial settings, increases in atmospheric acidity can dissolve carbonates (e.g., limestone, marble) in buildings and other structures, resulting in considerable aesthetic and economic damage (Figure 11.16). Archaeologists have estimated that acidic deposition damage in the last three decades to marble buildings of ancient Greece has been greater than the preceding 2400 years. Deterioration of stone products by acidic deposition is caused by (1) erosion and dissolution (e.g., dissolution and loss of material or surface details); (2) alterations (blackening of stone surfaces); and (3) spalling (cracking and cleaving of stone surfaces as a result of accumulations of alternation crusts). Painted surfaces can be discolored or etched by both wet and dry acidic deposition, and there may also be degradation of organic binders used to strengthen paints. A variety of other substrates are affected by acidic deposition (Table 11.4).

Several examples are available that describe the deterioration of different materials from acidic deposition. A marble column at the Field Museum in Chicago has eroded 10 mm in 70 years,

Table 11.4 Material Damage Due to Different Atmospheric Pollutants

Materials	Principal Pollutants	Impacts	Other Environmental Factors	Mitigation Measures
Metals	SO ₂ , other acid-forming gases	Corrosion, tarnishing	Moisture, air, salt, particulate matter	Surface plate or coat, replace with corrosion-resistant material, remove to controlled environment
Building stone	SO ₂ , other acid-forming gases	Surface erosion, soiling, black crust formation	Mechanical erosion, particulate matter, moisture, salts, temperature changes, vibrations, CO ₂ , microbes	Clean, impregnate with resins, remove to controlled environment
Ceramics, glass	Acid-forming gases, especially those containing fluoride	Surface erosion, surface crust formation	Moisture	Protective coatings, replace with more resistant materials, remove to controlled atmosphere
Leather	SO ₂	Weakening, powdered surface	Physical wear, residual acids introduced in manufacturing	Remove to controlled environment, consolidated with polymers, or replace
Paints, organic coatings	SO ₂ , hydrogen sulfide, O ₃	Surface erosion, discoloration, soiling	Moisture, sunlight, particulate matter, mechanical erosion, microbes	Repainting, replacement with more resistant materials
Paper	SO ₂	Embrittlement, discoloration	Moisture, physical wear, acidic materials introduced in manufacturing	Use synthetic coatings, store in controlled environment, deacidify, encapsulate, impregnate with organic polymers
Photographic materials	SO ₂	Microblemishes	Particulate matter, moisture	Remove to controlled atmosphere
Rubber	O ₃	Cracking	Sunlight, physical wear	Add antioxidants to formulation, replace with resistant materials
Textiles	SO ₂ and NO _x	Reduced tensile strength, soiling	Particulate matter, moisture, light, physical wear, washing	Replace, use substitute materials, impregnate with polymers
Textile dyes	NO _x , ozone	Fading, color change	Light, temperature	Replace, use substitute materials, remove to controlled environment

Source: U.S. EPA National Air Quality and Emissions Trends 1996 Report (U.S. EPA, 1996) and 2003 Report. Available at <http://www.epa.gov/air/airtrends/aqtrnd03/appenda.pdf>.

which is three times the *NAPAP erosion rate* determined in its studies. Statues erected at Gettysburg National Monument Park in the 1880s dissolved 10 times faster (approximately 8 to 9 mm/m of rain) where there were complex shapes as compared with flat, vertical objects. In the northeastern United States, corrosion rates for Cu and galvanized steel were 0.4 and 0.6 mm/year in rural areas and 0.9 and 1.5 mm/year in urban areas, respectively, which was due to increased exposure from SO₂ and acidity. Estimated damage due to acidic deposition to buildings in 17 northeastern and midwestern states has been reported at a level exceeding \$5 billion/year to repair mortar, galvanized



Figure 11.16 Acid structural damage. Evidence of acidic deposition and air pollution in the heavily industrialized Ruhr region of Germany, as shown by damage to a porous sandstone figure over the portal of a 1702 castle. The figure on the left was taken in 1908 and shows evidence of weathering over 206 years with the loss of the left hand. In 1968, after 60 more years of weathering, the structure (figure on the right) shows there was rapid deterioration with the loss of the right hand, face, and all of the fine-crafted features. (Photographs courtesy of Herr Schmidt-Thomsen.)

steel, stone structures, and for repainting. Additionally, billions of dollars are also associated with damages to vehicle paint, roofing materials, concrete, and other exposed materials.

11.3.5 Ecosystem Effects of Acidic Deposition

Acidic deposition can result in a variety of environmental impacts on different ecosystems. Prior to discussing the mechanisms involved and some approaches to reversing the effects of acidification, it is important to examine the nature of acidity in soil, effects to vegetation, and aquatic environment impacts. In many natural systems, the damage from acidification is often not directly due to the presence of excessive H^+ , but is instead caused by changes in other elements when the system becomes more acidic (e.g., pH decreases). Examples include increased solubilization of metal ions that can be toxic to plants and animals such as Al^{3+} and some trace elements (e.g., Cu^{2+} , Mn^{2+} , Pb^{2+}), more rapid losses of basic cations (e.g., Ca^{2+} , Mg^{2+}), and the creation of unfavorable soil environments for soil microorganisms important in many nutrient cycles. Acid precipitation research requires the sampling of rain water and acidic particulates.

11.3.5.1 Soils

Acidic deposition results in the addition of strong acids to soils. Under certain conditions this can result in the *leaching of basic cations* (Ca^{2+} and Mg^{2+}) and an *increased solubility of Al^{3+}* . The inorganic and organic chemistry of this system is, however, highly complex (Figure 11.17); despite

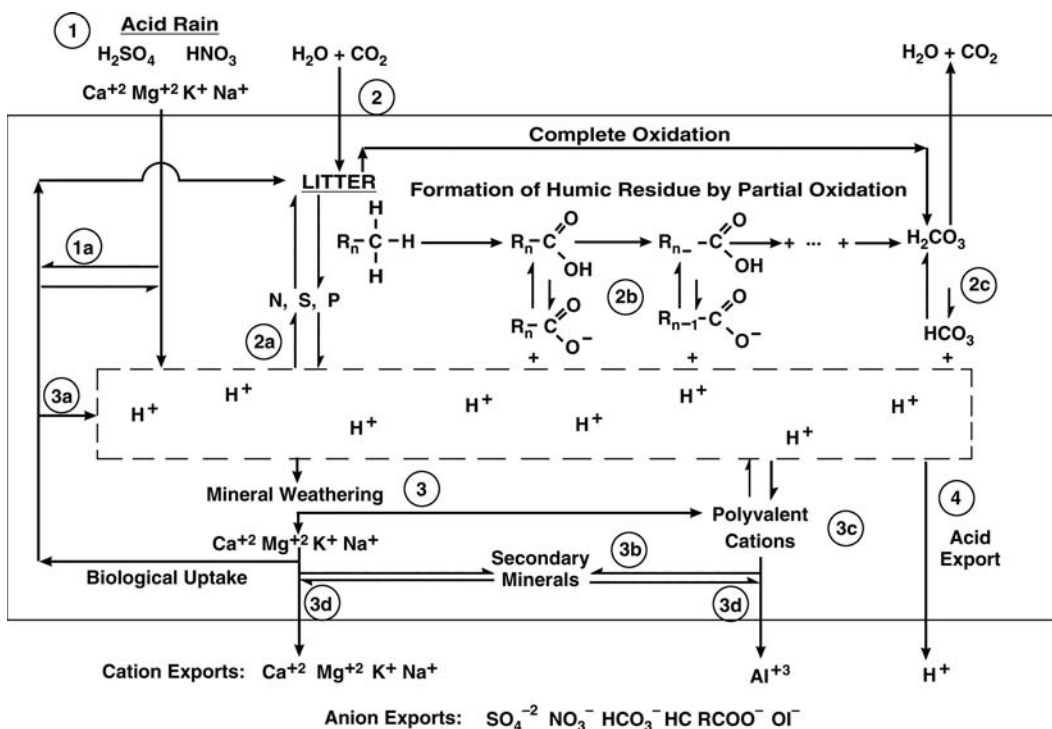


Figure 11.17 Effects of acidic deposition on soils. (1, 1a) Inputs of acid rain add H^+ , acidic anions, and basic cations; (2) biological processes such as mineralization (2a) of C, N, S, P produce H^+ and also form weak organic acids that can consume H^+ (2b) or ultimately result in loss of H_2O and CO_2 from soil following complete oxidation (2c); (3) weathering of primary minerals produces cations for (3a) plant uptake, (3b) secondary minerals, (3c) acidic, and (3d) basic cations; (4) export of positive charge from soils as leachable cations (H^+ , Al^{3+} , Ca^{+2} , Mg^{+2} , K^+ , Na^+) must be balanced electrically by anion export (SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- , organic acids). (Adapted from Krug and Frink, 1983.)

extensive research efforts, much remains to be learned about the specific mechanisms involved and the situations where acidic deposition has a significant environmental impact. In a practical sense, acidic deposition will have a greater effect on forest soils than on agricultural or urban soils because in the latter situations we routinely and inexpensively counteract the effects of all acidifying processes by *liming* (e.g., addition of CaCO_3). Forest soils have been frequently limed in some European countries; Sweden spends millions of dollars annually distributing lime to mitigate acid precipitation impacts. The logistics and cost often preclude liming as a routine management practice except in areas severely affected by acidic deposition, extensively managed lands, or areas that are deemed important for different reasons.

Example Problem 11.4

A soil has an exchangeable Al^{3+} acidity of 20 mmol/kg at pH 4.5. We want to add enough liming material to the site to reduce the exchangeable Al^{3+} acidity to 5 mmol/kg. How much CaCO_3 would be needed to neutralize this amount of acidity? First, we must calculate the concentration of Al acidity that must be neutralized, i.e.,

$$20 \text{ mmol/kg} - 5 \text{ mmol/kg} = 15 \text{ mmol/kg}$$

A mole of CaCO_3 can neutralize 2 mol of H^+ that originates from Al acidity due to hydrolysis reactions. Because 1 mol of CaCO_3 weighs approximately 100 g, we will need 50 g to neutralize each mole of

acidity (or 50 mg/mmol acidity). If we assume the amount of soil required to be amended at the site is approximately 2,240,000 kg/ha, we can determine the amount of CaCO_3 needed by first calculating the amount of acidity to be neutralized as

$$\frac{2.24 \times 10^6 \text{ kg}}{\text{ha}} \times \frac{15 \text{ mmol}}{\text{kg}} = \frac{33.6 \times 10^6 \text{ mmol}}{\text{ha}}$$

and then determining the kg of CaCO_3 needed by

$$\frac{33.6 \times 10^6 \text{ mmol}}{\text{ha}} \times \frac{50 \text{ mg CaCO}_3}{\text{mmol}} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = \frac{1680 \text{ kg CaCO}_3}{\text{ha}}$$

Now consider how much CaCO_3 would be needed per hectare to neutralize the acidity of 100 cm (1 m) of rain with a pH of 4.0.

$$\begin{aligned} \frac{10,000 \text{ m}^3}{\text{ha}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{0.0001 \text{ mol H}^+}{\text{L}} \times \frac{50 \text{ g CaCO}_3}{\text{mol H}^+} \\ = \frac{50,000 \text{ g (or 50 kg) CaCO}_3}{\text{ha}} \end{aligned}$$

The rate and extent of increased acidification beyond that caused by naturally acidic rainfall depend both on *soil buffering capacity* and the use of the soil. The issue is complicated by the fact that many areas subjected to the greatest amount of acidic deposition are also areas where considerable natural acidification occurs. For example, forested soils in the northeastern United States are developed on highly acidic, sandy parent material that has undergone tremendous changes in land use in the past 200 years that contributed to natural acidification. However, clear-cutting and burning by the first Europeans to settle in the area have been almost completely reversed and many areas are now totally reforested. Soil organic matter that accumulates with reforestation represents a natural source of acidity and pH buffering. Similarly, greater leaching or depletion of basic cations by plant uptake in increasingly reforested areas must consider the significant inputs of these same cations in precipitation. Many studies have examined the changes in chemical properties of soils following long-term acidic deposition and changing land-use patterns. For example, acidic deposition has accelerated the leaching of base cations at Hubbard Brook Experimental Forest in New Hampshire, resulting in a 50% decline in the available soil Ca^{2+} pool over the past 50 years.

11.3.5.2 Agricultural Crops

A 1979 report by the United States and Canada Research Consultation Group stated that “there is every indication that acid rainfall is deleterious to crops” and that there is “the potential for widespread economic damage to a number of field crops.” Impacts to agricultural ecosystems, however, have been minor, and, in fact, acidic deposition at times has been shown to be beneficial. *Direct impacts* would be associated with aboveground plant communities, whereas indirect effects could be manifested through degradation of soil quality. *Ozone pollution*, which often accompanies atmospheric acid substances, is thought to be primarily responsible for crop damage. Ozone crop damage is especially problematic at 0.10 ppmv O_3 levels (when compared to 0.025 ppmv O_3 levels), with crop yield losses ranging from <20% (kidney beans, corn, wheat, and cotton under drought conditions), 20 to 50% (soybeans, spinach, and cotton under irrigated conditions), and >50% (peanuts, lettuce, and turnips).

Acidic deposition contains N and S, which are important *plant nutrients*. Therefore, foliar applications of acidic deposition at critical growth stages can be beneficial to plant development and reproduction. Generally, controlled experiments require the simulated acid rain to be pH 3.5 or less in order to produce plant injury. Remember that unpolluted rainfall has a pH of about 5.6, which suggests that the amount of acidity needed to damage some plants is 100 times greater than natural rainfall. Crops that responded negatively (e.g., decreased growth and yields) in simulated acid rain studies have included garden beets, broccoli, carrots, mustard greens, radishes, and pinto beans; however, there are cultivar differences among the different crops. Positive responses to acid rain have been identified with alfalfa, tomato, green pepper, strawberry, corn, lettuce, and some pasture grass crops; again, there are cultivars of each crop that show no response to the simulated acid rain tests.

As mentioned earlier, most agricultural lands are maintained at pH levels that are optimal for crop production. Ideally, soil pH should be in the pH 6.0 to 7.0 range; however, pH levels of organic soils are usually maintained at pH 5.0 to 6.0. Because agricultural soils are generally well buffered, the amount of acidity derived from atmospheric inputs is not sufficient to alter their overall soil pH significantly. Nitrogen and S soil inputs from acidic deposition can be beneficial, and with the reduction in S atmospheric levels mandated by *1990 amendments to the Clean Air Act*, the S fertilizer market has grown, according to the Sulfur Institute. The amount of N added to agricultural ecosystems as acidic deposition is rather insignificant in relation to the 100 to 300 kg N/ha/year required by agricultural crops; forest ecosystems have lower N requirements. It is generally assumed that acidic deposition is unlikely to affect properly managed agricultural ecosystems and that the N and S additions are beneficial. Unfortunately, forest ecosystems in the eastern United States, Rocky Mountains, and California are developing symptoms of N saturation due to increased N added through acidic deposition (U.S. EPA, 2002), as discussed in the next section.

11.3.5.3 Forest Ecosystems

Perhaps the most publicized and visible issue related to acidic deposition has been its effects on forest vegetation. *Widespread forest decline* has been reported in areas where significant acidic deposition has occurred. In Europe, it has been estimated that as much as 35% of all forests have been affected by acidic deposition. Similarly, in the United States many important forest ranges such as the *Adirondacks* in New York, *Green Mountains* in Vermont, *Great Smoky Mountains* in North Carolina, and areas in Pennsylvania have experienced sustained decreases in tree growth for several decades and show serious visible damage. As noted earlier, conclusive evidence that forest decline or dieback is caused solely by acidic deposition has been limited, which is complicated by the many known interactions between acidification and other environmental or biotic factors that influence tree growth. However, it is known that O_3 can cause crop and tree damage, and research has confirmed that acidic deposition has contributed to a decline in high-elevation red spruce and sugar maple in the eastern United States. In addition, N saturation of forest ecosystems from atmospheric N deposition is believed to result in increased plant growth, which in turn increases water and nutrient use followed by deficiencies that can cause chlorosis and premature needle drop as well as increased leaching of base cations from the soil environment. The following provides a brief summary of some means by which acidic deposition can directly affect trees and other plants (Figure 11.18); indirect effects on plant growth due to soil acidification, as summarized in Section 11.3.5.1, can also be significant.

Wet and dry acidic deposition on leaves and needles may enter directly through plant stomates. If the deposition is sufficiently acidic (pH ~3.0), damage can also occur to the waxy cuticle on the surface of leaves and needles, increasing the potential for direct injury of exposed leaf mesophyll cells. *Foliar lesions* are one of the most common symptoms of plants subjected to simulated acidic precipitation. Gaseous compounds such as SO_2 and SO_3 present in acidic mists or fogs can also enter leaves through the stomates, form H_2SO_4 upon reaction with H_2O in the cytoplasm of leaf

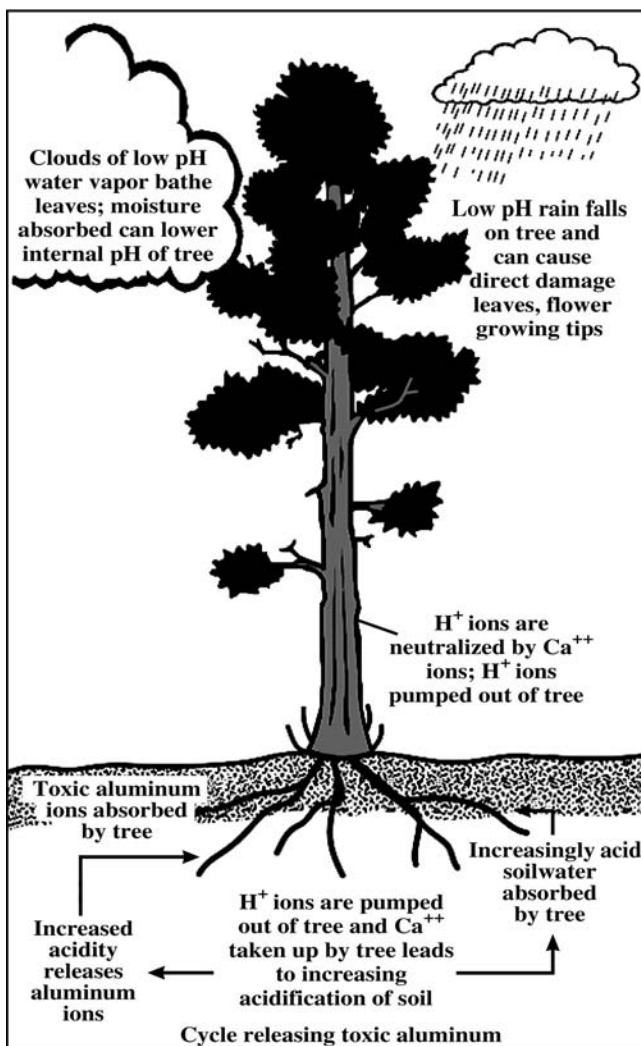


Figure 11.18 Effects of low-pH rainfall and trees in soil acidification processes. In soils with inorganic Al-to-Ca ratios of greater than 1.0, competition between these two species favors Al. Because Ca is a secondary nutrient required for tree growth, low-pH soils and increased Al:Ca levels can result in decreased forest health. (From Bush, M. B., *Ecology of a Changing Planet*, Prentice Hall, Upper Saddle River, NJ, 1997. With permission.)

cells, and disrupt many pH-dependent metabolic processes. Several studies have shown increased necrosis of leaves and needles when exposed to high levels of SO_2 gas. The exact mechanisms by which acidification of leaf cells cause injury are not completely known and certainly vary among plant species. *Physiological changes* associated with exposure to simulated acidic deposition include collapsed epidermal cells, eroded cuticles, loss of chloroplast integrity and decreased chlorophyll content, loosening of fibers in cell walls and reduced cell membrane integrity, and changes in osmotic potential that cause a decrease in cell turgor.

Considerable research has been directed at the secondary effects on vegetation exposed to acidic deposition, specifically the likelihood of *increased disease or insect damage*. The general hypothesis is that any injury to a leaf surface will promote the survivability of pathogenic organisms and their entry into the plant. Studies have shown that leaves exposed to acidic precipitation are more “wetable,” a key condition for the establishment of a pathogenic population. Lesions on acidified leaf surfaces are openings that permit ready entry of plant pathogens, in much the same manner

as natural wounds. Other effects of acidic deposition on leaves may also predispose them to disease or insect damage. Leaching of nutrients and organic compounds and disruption of photosynthesis and nutrient metabolism weaken the resistance of the plant to any type of stress.

There may also be an increased likelihood of root diseases. In addition to the damages caused by exposure to H_2SO_4 and HNO_3 , roots can be directly injured or have their growth rate impaired by increased concentrations of soluble Al^{3+} and Mn^{2+} in the *rhizosphere*. *Root exudates* (organic compounds secreted from plant roots) have been shown to increase when aboveground plant metabolism is affected by acidic deposition on leaves and stems. Changes in the amount and composition of these exudates can then alter the activity and population diversity of soil-borne pathogens. The general tendency associated with increased root exudation is an enhancement in microbial populations due to an additional supply of carbon (energy). Chronic acidification can also alter nutrient availability and uptake patterns, and thus aboveground plant growth and yield.

Long-term studies conducted at the *Hubbard Brook Experimental Forest* in New Hampshire suggest acidic deposition has resulted in significant leaching of basic cations that are important for acid neutralization and plant nutrition. Consequently, forest growth and biomass production of primarily *red spruce trees in the White Mountains* have dropped to approximately zero since 1987; leaching of cellular Ca^{2+} from red spruce foliage has made these trees susceptible to freezing. With the decrease in acidic deposition and reduction in about 80% of the airborne basic cations (mainly Ca^{2+} but also Mg^{2+}) from 1950 levels, researchers at Hubbard Brook suggest forest growth has slowed because soils are not capable of weathering at a rate that can replenish these essential plant nutrients (Figure 11.18). *Sugar maple trees* in Pennsylvania have succumbed to extensive mortality due to Ca^{2+} and Mg^{2+} deficiencies that have resulted from acidic deposition leaching these soil base cations. In Germany, acidic deposition was implicated in the loss of soil Mg^{2+} as an accompanying cation associated with the downward leaching of SO_4^{2-} , which resulted in forest decline. Several European countries have used helicopters to fertilize and lime forests in an effort to improve forest health.

11.3.5.4 Aquatic Ecosystems

Ecological damage to freshwaters from acidic deposition is a serious and increasingly well-documented global problem. As with forests, the weight of scientific evidence suggests that a number of interrelated factors associated with acidic deposition are responsible for many of the undesirable changes occurring in aquatic ecosystems. *Acidification of freshwaters* is, however, not a new phenomenon. Studies of lake sediments suggest that increased acidification began in the mid-1800s, although the process has clearly accelerated since the 1940s. Current studies indicate there is significant S mineralization in forest soils affected by acidic deposition and that the SO_4^{2-} levels in adjacent streams remain high, despite a decrease in the amount of atmospheric S deposition. Intensive scientific research on aquatic ecosystems has been conducted since the early 1970s, resulting in hundreds of technical papers and dozens of comprehensive books on the subject (see the references section of this chapter). The subject is complex, and the magnitude of the effects of acidic deposition on freshwaters has been shown to vary widely among geographic regions.

Geology, soil properties, and land use are the main determinants of the effect of acidic deposition on aquatic chemistry and biota, as shown in Table 11.5 for two European watersheds. Lakes and streams located in areas with calcareous geology (e.g., limestone) resist acidification more than those where granite and gneiss are the predominant geologic materials. Soils developed from calcareous parent materials also tend to be deeper and more buffered against acidification than the thin, acidic soils common to granitic areas.

Land management also affects freshwater acidity. Forested watersheds tend to contribute more acidity than those dominated by meadows, pastures, and agronomic ecosystems. Trees and other vegetation in forests have been shown to “scavenge” (retain on leaves and stems) acidic compounds in fogs, mists, and atmospheric particulate matter. These acidic compounds are later delivered to

Table 11.5 Chemical Properties of Precipitation, Throughfall, Leachate, and Stream Waters in Two European Watersheds

Watershed Description	pH	H ⁺	Ca ²⁺	Total SO ₄ ²⁻	Al (μg/L)	
					Total	Soluble
Loch Chon (Scotland) — Subject to high acidic deposition; rainwater partially neutralized by vegetation and in soil profile; leachate strongly influenced by calcium-rich geology; streams support fish						
(meq/m ² /year)						
Input						
Above canopy	—	48	—	132	—	—
Below canopy	—	24	—	138	—	—
(μeq/L) (mg/L)						
Concentration						
Precipitation	4.5	29	11	53	—	—
Throughfall	4.8	15	50	92	—	—
Leachate from O horizon	4.2	68	—	122	—	—
Leachate from BC horizon	4.4	37	—	89	—	—
Stream water	5.1	8	72	93	129	47
Kelty (Scotland) — Large inputs of sulfate and acidic deposition; spruce canopy contributes to acidification; high sulfate uptake by trees, but little buffering of acidity by soils and geologic material; many streams cannot support fish						
(meq/m ² /year)						
Input						
Above canopy	—	72	—	140	—	—
Below canopy	—	80	—	230	—	—
(μeq/L) (mg/L)						
Concentration						
Precipitation	4.5	29	11	53	—	—
Throughfall	4.2	57	45	164	—	—
Leachate from O horizon	4.0	100	—	115	—	—
Leachate from BC horizon	4.1	80	—	73	—	—
Stream water	4.5	34	48	93	140	62

Source: Mason, B.J., *Acid Rain: Its Causes and Effects on Inland Waters*, Oxford University Press, New York, 1992. With permission.

forest soils when rainfall leaches them from the surfaces of the vegetation. Rainfall below forest canopies (e.g., *throughfall*) is usually more acidic than ambient precipitation. Silvicultural operations that disturb soils in forests as part of planting, fertilizing, draining, and harvesting trees can increase acidity by stimulating the oxidization of organic N and S, and reduced-S compounds such as FeS₂. Conversely, runoff and leachate from watersheds dominated by well-limed agricultural soils can act to neutralize acidity in lakes and streams. Other factors that can influence freshwater acidification include rainfall intensity and duration, topography, and hydrogeology, all of which act to determine the direction and rate of water flow (and thus acidic compounds) through soils and parent material to freshwaters.

A number of ecological problems arise when freshwaters are acidified below pH 5.5, and particularly below pH 4.0. Decreases in *biodiversity* (number of different species present) and *primary productivity* (actual numbers and biomass) of phytoplankton, zooplankton, and benthic

invertebrates commonly occur (Figure 11.19). Decreased rates of biological decomposition of organic matter can lead to reduced supply of nutrients as mineralization slows. Microbial communities may also change, with fungi predominating over bacteria. Proposed mechanisms to explain these ecological changes center around physiological stresses caused by exposure of biota to higher concentrations of Al^{3+} , Mn^{2+} , and H^+ and lower amounts of available Ca^{2+} . One specific mechanism suggested involves the disruption of ion uptake and the ability of aquatic plants to regulate sodium (Na^+), K^+ , and Ca^{2+} export and import from cells.

Acidic deposition can also affect fish, amphibians, and mammals. Widespread evidence exists for *declining fish populations* in acidified lakes and, under conditions of extreme acidity, of fish kills (Figure 11.19). In general, if the water pH remains above 5.0, few problems are observed; from pH 4.0 to 5.0 many fish are affected, and below pH 4.0 few fish can survive. The major cause of fish kill is the direct toxic effect of Al^{3+} , which interferes with the role Ca^{2+} plays in maintaining *gill permeability* and thus *respiration*. Aluminum toxicity can be a serious problem and can result in major fish kills if any climatic condition, such as heavy rains or rapid snowmelt, substantially accelerates the flow of Al^{3+} -laden water to streams or lakes within the watershed. Calcium has been

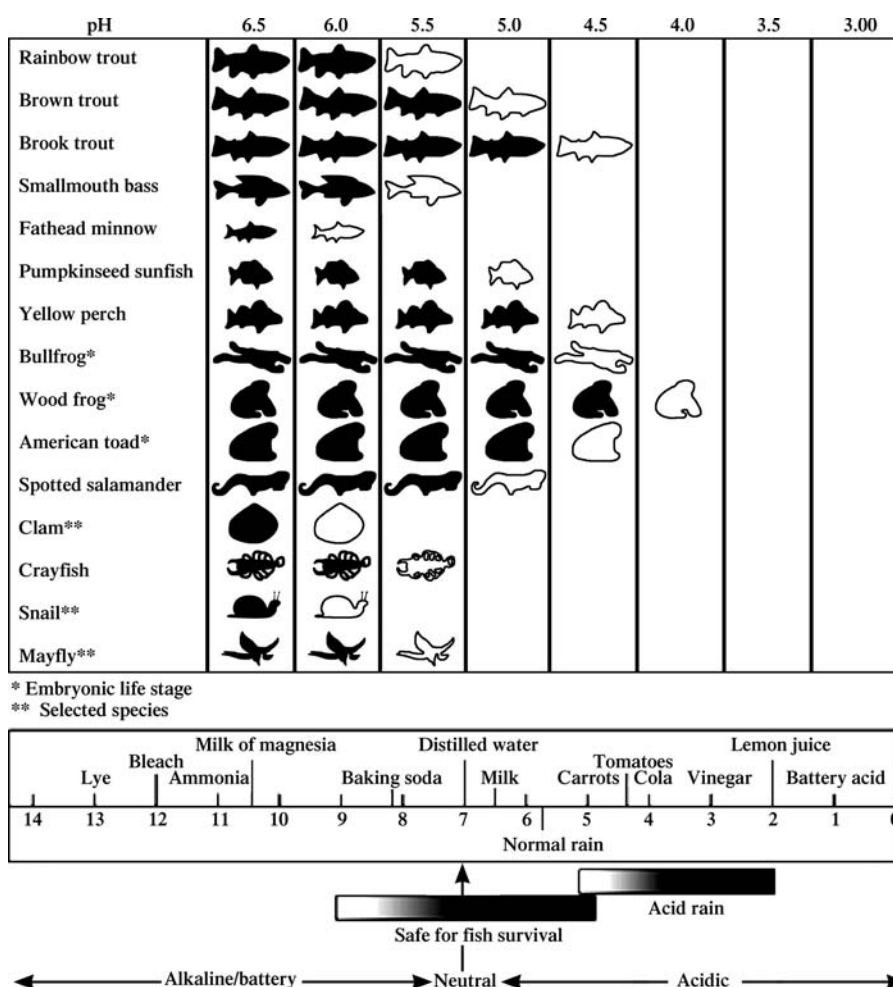


Figure 11.19 Examples of the sensitivity of aquatic species to different pH levels. Note that the solid image represents a pH level that the aquatic species survives and the species outline indicates conditions unfavorable for survival. Examples of various substances and their pH levels are also shown for comparison. (From Bush, M. B., *Ecology of a Changing Planet*, Prentice Hall, Upper Saddle River, NJ, 1997. With permission.)

shown to mitigate the effects of Al^{3+} , but in many acidic lakes Ca^{2+} levels are inadequate to overcome Al^{3+} toxicity. Low pH values also disrupt the Na^+ status of blood plasma in fish. Under very acidic conditions, H^+ influx into gill membrane cells both stimulates excessive efflux of Na^+ and reduces influx of Na^+ into cells from external waters. Excessive loss of Na^+ can cause mortality in fish. *Other indirect effects* of acidification on fish survival include reduced rates of reproduction, high rates of mortality early in life or in reproductive phases of adults, and migration of adults away from acidic areas. Amphibians are affected in much the same manner as fish, although they are somewhat less sensitive to Al^{3+} toxicity. Birds and small mammals often have lower populations and lower reproductive rates in areas adjacent to acidified freshwaters. This may be due to a shortage of food due to smaller fish and insect populations or to physiological stresses caused by consuming organisms with high Al^{3+} concentrations.

11.3.6 Reversing the Effects of Acidic Deposition

The environmental damage caused by acidic deposition will be difficult and extremely expensive to correct. In the long term, reversal of these effects can only begin to be accomplished by reducing S and N emissions (Driscoll et al., 2001). Some approaches to achieve this include burning less fossil fuel; using cleaner energy sources (e.g., low-S coal or wind and solar systems); and designing more efficient “scrubbers” to reduce the amount of these gases emitted by utilities, industries, and vehicles. There is a general consensus among the scientific community that reducing emissions will result in slow, but eventual improvement in acidified ecosystems, particularly freshwaters. For the present, despite the firm conviction of most nations to reduce acidic deposition, it appears that the staggering costs of such actions have delayed complete implementation of this approach. The U.S. Congress estimated that to reduce SO_2 emissions alone by 9 million Mg (10 million tons) would cost as much as \$3.6 billion over a 5-year period; the EPA estimated that 20-year costs could be as much as \$33 billion. *Annual costs* associated with damage attributed to acidic deposition impacts to structural, ecological, and environmental systems in the northeastern United States have been approximated to be \$5 billion due to corrosion of buildings, bridges, and other structures (\$2 billion), forest ecosystem damage (\$1.75 billion), agricultural ecosystems impacts (\$1 billion), and loss of tourism and fishing revenue (\$0.25 billion). The *1990 amendments to the Clean Air Act* are expected to reduce acid-producing air pollutants, e.g., SO_2 and NO_x , which are common contaminants released in energy-related operations such as electric power plants. One cleanup method implemented in the 1990 Amendments was that of emission allowances that set the amount of S that can be emitted by a utility. The allowances are based on the historical fuel use and SO_2 emissions of a utility, with each allowance representing 1 ton of SO_2 that can be bought, sold, or banked for future use.

Short-term remedial actions for acidic deposition are available and have been successful in some ecosystems. *Liming of lakes and some forests* (also fertilization with trace elements and Mg^{2+}) has been practiced in European counties for more than 50 years and is now done in other areas of the world. Hundreds of Swedish and Norwegian lakes have been successfully limed in the past 30 years. The effectiveness of liming depends mainly on the residence time of water in the lake. Lakes with short mean residence times (see Chapter 2) for water retention may need annual or biannual liming; lakes with long mean residence times may need liming every 5 or 10 years. As an example, ten small Adirondack lakes were limed in 1983 to 1984, and the percent survival of brook trout increased from about 10% at pH 4.5 to 60 to 80% at pH 5.5 to 6.5. By 1986, however, three of the limed lakes were sufficiently reacidified to cause significant declines in fish populations. The logistics of liming lakes and forests are formidable. Aerial application of lime via planes and helicopters is often required; hence, application costs often far exceed the expense of the liming materials. Liming may have some negative effects as well. Much of the vegetation in forested areas is well adapted to acidic soils; liming (or overliming) may alter the distribution of species in these ecosystems in an unpredictable and perhaps undesirable manner.

Environmental Quality Issues/Events

Restoration Efforts of an Industrial Region Affected by Sulfur Dioxide, Heavy Metals, and Acidic Deposition: Sudbury, Canada

The *Sudbury region* in Canada, located about 200 km east of the upper peninsula of Michigan, has the largest known concentration of minable nickel (Ni) ore in the world, estimated at 20 million Mg. Sudbury ore also contains significant economic levels of Cu, gold (Au), iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), ruthenium (Ru), selenium (Se), silver (Ag), and tellurium (Te), as well as trace amounts of arsenic (As), cobalt (Co), Pb, and Zn. Minerals in the ore are primarily sulfides with high-grade ores yielding 7 to 10% Cu and Ni combined.

Sudbury mineral resources were discovered during the construction of the Canadian transcontinental railway in 1883. In 1888, the first roast yard and smelting operation was established in the area and used to obtain Cu; at that time Ni was considered an impurity. The roasting process involved piling crushed ore on logs and burning the material for 2 months. The intensity of the fire resulted in ore combustion that caused the oxidation of sulfides and release of gaseous SO₂. There were 11 roast yards used during 1888 to 1929, with most of the yards located near the nine smelters that operated in the Sudbury region. Practically all the woody materials in the general vicinity of the roast yards were used in the roasting process. Because an estimated 10 million Mg of SO₂ were released at ground level from the roasting yards, it has been suggested that the extensive destruction of vegetation and toxic soils was due to these early activities.

Smelting operations, however, resulted in much more widespread damage to the surrounding ecosystem because the fumes contain Ni and Cu particles and significant amounts of SO₂. It was realized in the early 1940s that smelter emissions had caused extensive damage to the forests in the Sudbury region. Smoke from the smelters could be seen 120 km away and the smell of S was noticed at least 60 km from the source emissions. Zones of damage around the three major smelters were described in the earlier 1970s as either barren areas that amounted to approximately 17,000 ha or large, semibarren areas surrounding the barren areas, which were estimated to be another 72,000 ha. It has also been suggested that more than 7000 lakes within the Sudbury region were affected by pollutants derived from smelting activities.

The environmental damage due to mining and processing the Sudbury region ore is probably the most highly recognized destruction of a North American ecosystem; Noril'sk in central Siberia is considered the world's most polluted area (10,000 km²) and the largest point source of SO₂. Sudbury damage is the result of impacts related to activities that occurred over more than 100 years, and involved SO₂ and trace elements (Cu, Ni, Al) that combined create low-pH environments with highly bioavailable toxic metals (see Chapters 7 and 9 for further details). The 1960s brought about an intense pressure to reduce S emissions from smelting operations and in the 1970s there was a rapid decline in the amount of S that affected local air quality. Measures that resulted in improved air quality included construction of the world's tallest smokestack (381 m) to increase the dispersal of smelter emissions, closure of some of the older smelting and processing plants, reducing S emissions, and halting smelter operation during weather conditions that did not allow dispersal of emission plumes.

During the 1970s and 1980s, several studies were conducted to evaluate terrestrial and aquatic recovery due to the reduction in S and trace element pollution. While the recovery was slower than expected, primarily because of SO₂ fumigation (e.g., high SO₂ concentrations in localized areas) caused by climatic conditions and long-term consequences of high acidity and toxic metals, changes were apparent particularly in areas of minor pollution. Fertilization, liming, and introduction of new plant species with acid or metal tolerances have accelerated the recovery process. Liming was found to be important for increasing the soil pH, forming Ni and Cu precipitates, reducing metal uptake due to increased Ca²⁺ and Mg²⁺ competition, and preventing Al³⁺ toxicity. One of the goals for the revegetation program was to use minimal amounts of amendments and low seeding rates so that increased plant colonization and diversity of native species would occur. Aspen trees appear to be rapidly invading the test sites with birch trees following liming treatments. Other plant species indigenous to the Sudbury region that are revegetating treated lands include oaks, willows, and various wildflowers and grasses. Over time, there has been evidence of plant succession and there is hope that biotic communities are adapting to the changing soil and environmental conditions and that they will ultimately produce a diverse ecosystem.

Significant lake impacts due to smelter operations included losses of sport fish species such as lake trout, brook trout, and smallmouth bass, the aquatic trophic level species zooplankton, phytoplankton, and benthic invertebrates, as well as waterfowl and amphibians. Liming of Sudbury lakes resulted in aquatic habitat improvements via increased pH and reduced toxic element concentrations. Lakes that have been limed and stocked with bass and lake trout have shown promise for the recovery of recreational sportfishing activities. In addition, with increases in fish populations and invertebrate prey, the breeding habitats for waterfowl have improved, and as the ecosystem improves, aquatic species, plants, and animals are expected to increase with the reduction in S and trace element emissions.

Although more than \$1 billion has been spent on reducing S emissions and environmental restoration activities, there is still much to be done in the Sudbury region. Both industry and municipalities have worked together to revegetate more than 4000 ha of barren lands and have planted more than 3 million trees. Additional improvements will undoubtedly be made to the affected aquatic ecosystems by more liming programs that bring the pH levels of affected lakes to near 6.0. The enormous efforts that have been expended to improve the environmental quality of the region over the past 25 years have resulted in Sudbury being named one of Canada's ten best cities according to a prominent Canadian magazine. More noteworthy was the Government's Honor Award received in 1992 at the United Nation's Earth Summit in Rio de Janeiro, Brazil, which recognized the outstanding achievements attained with the Sudbury municipal land reclamation program.

— Source: Gunn (1995)

PROBLEMS

- 11.1 For each of the major greenhouse gases, describe measures that might be taken to reduce atmospheric concentrations. How would these measures affect society?
- 11.2 For a fictitious greenhouse gas with a global warming potential (GWP) of 50 and an annual emission of 5 Tg, calculate the million metric ton carbon equivalent (MMTCE) value and compare it with those for CO₂, CH₄, and N₂O.
- 11.3 If soils could potentially sequester 40 Pg of C from the atmosphere over the next 50 years, what fraction or percentage of the total C in the atmosphere does this represent?
- 11.4 In 2001, the United States released the equivalent of 98 MMTCE of N₂O into the atmosphere. Convert this to Tg CO₂ Equivalent.
- 11.5 How many gigatons (Gt) of C are there in 1 MMTCE?
- 11.6 If 1 ha of land could sequester 300 kg C, how many hectare would it take to sequester 10% of the C emitted as CO₂ each year?
- 11.7 Describe the difference between the following terms: acid rain, acid precipitation, acid deposition, acid-forming substances, acidity.
- 11.8 What are the primary sources that contribute to acidic deposition? Where are these sources located? What forms of atmospheric substances are released from these sources?
- 11.9 Calculate the difference in rainwater acidity between that of the Rocky Mountains (pH = 6.0) and rainfall in Florida (4.7), Tennessee (4.5), and Ohio (4.2).
- 11.10 There are several reasons acid soils are harmful to plants, animals, and possibly humans. What are some of the problems associated with acid soils, how are they manifested, and what can be done to correct these problems?
- 11.11 Determine the amount of liming material (e.g., CaCO₃) that would be required to neutralize the acidity in each of the following examples:
 - a. 25 mmol/kg exchangeable Al³⁺ acidity
 - b. 20 mmol/kg exchangeable H⁺ acidity
 - c. 10 mmol/kg organic acid acidity
- 11.12 Why have forest ecosystems been affected more by acidic deposition than agricultural ecosystems? What is N saturation and why might it be a greater concern in the future?

- 11.13 If a lake containing 3 million m³ of water has a pH of 4.50, what is the amount of acidity (H⁺) that would need to be neutralized if the lake pH were to be limed to a pH of 5.60? How much pure CaCO₃ would be required to neutralize the acidity?
- 11.14 Describe various methods that can be implemented to restore damaged soils, forests, and lakes. List some potential problems that could occur in these ecosystems if the restoration practices do not consider the impacts that may result from altering the whole ecosystem.
- 11.15 Use the data in Table 11.3 to hypothesize why NO_x and SO₂ have increased in the United States since 1900. What may have caused the increases and decreases in concentrations during the 20th century?

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PART IV

Contaminant Assessment and Remediation

Remediation of Soil and Groundwater

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12.1 INTRODUCTION

Remediation refers to processes or methods for treating contaminants in soil or water such that they are contained, removed, degraded, or rendered less harmful. Contaminated waters are generally associated with groundwater drinking supplies that require remediation, although removal of substances from contaminated surface waters is also common. There are several subcategories of remediation. *Site remediation* is often used for processes that contain (i.e., restrict movement) a contaminant but do not necessarily directly affect the contaminant, whereas *soil or water remediation* generally refer to processes that directly treat the medium and affect the contaminant in some way. *In situ remediation* refers to treatment of soil or water in place; *ex situ remediation* involves physical removal and treatment of either soil or water on-site or at another location.

There are numerous reasons a remedial action may be necessary. The most obvious is that the soil or water has been contaminated and the natural inclination is to return that resource to its original, uncontaminated state. The implication is that the contamination may cause or is causing harm (we would call it pollution if it was actually causing harm) to some organism. Of course, not all contaminated sites are remediated just because they are contaminated. Three common reasons for remedial action are (1) a risk assessment that suggests an unacceptable level of risk (see Chapter 13); (2) direct evidence of human or ecological harm; and (3) regulatory limits for contaminant concentrations in soil, food, or water are exceeded. A human health risk assessment will use some guidelines for exposure that may suggest remediation is warranted. For noncarcinogenic substances, the anticipated dose of the contaminant may exceed the reference dose for that substance, or the

cancer risk assessment may exceed the 10^{-4} to 10^{-6} risk guidelines for a potential carcinogen. An ecological risk assessment may suggest that soil or water contaminant concentrations exceed a toxicological threshold for one or more species. Direct evidence of human or ecological harm might include blood Pb concentrations in children that exceed a critical value or the lack of vegetation on a contaminated site. Regulatory limits that could trigger the need for remediation include soil that fails the *toxicity characteristic leaching procedure* (TCLP) test (developed to assess the potential for metals to leach into groundwater) or contaminant concentrations in groundwater that exceed the *maximum contaminant levels* (MCLs) for drinking water purposes (see Chapters 2 and 4).

The *Superfund* process provides a mechanism for the possible cleanup of contaminated sites. An abbreviated version is presented in Figure 12.1. Site discovery can come about in a variety of ways. Routine testing of drinking water, for example, may turn up unacceptable concentrations of contaminants and the source of the contamination must be located. Once the source is found, a preliminary assessment is performed to determine the nature and extent of the contamination. *Principal responsible parties* (PRPs) are also identified. If there is a strong likelihood that the site will require remediation, it will be placed on the *National Priorities List* (NPL). Often there is opposition to a site being “listed” as there is a stigma associated with a Superfund site. The NPL and information on each site are available from the U.S. EPA on the Internet (see list of Supplementary Materials).

The remedial investigation/feasibility study is a much more detailed examination of the site that includes risk assessments and suggestions of remedial alternatives. The PRPs are actively

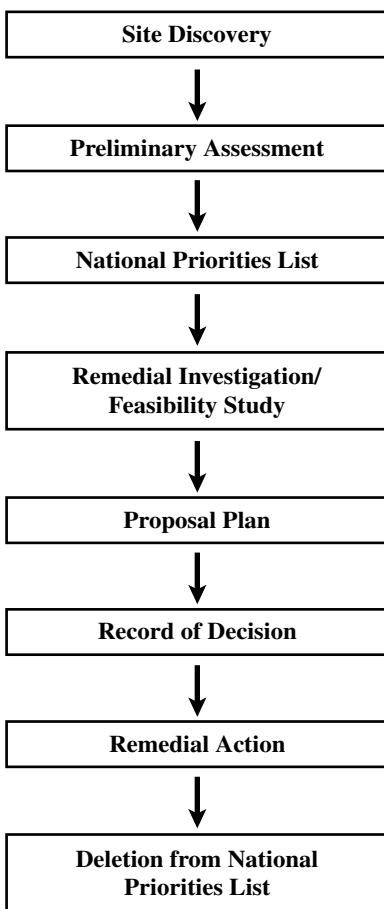


Figure 12.1 Flow diagram for the Superfund process.

involved at this point. The proposed plan is a listing of all possible options for remediation (including no action) with cost estimates, how each addresses the human and ecological risks, and the preferred alternative. The record of decision (ROD) follows and represents the actual plan that will be used for the remediation. The remedial action then takes place and includes a post-treatment assessment of the effectiveness of the remediation, generally after 5 years. If the remedial action successfully addresses the risk, the site will be removed from the NPL. The bulk of the work is performed by contractors who are paid by the EPA, states, and/or the PRPs. Each step generates documentation that is subject to a public comment period before it is accepted. The general public has many opportunities for input and the EPA may provide funds for technical advice for citizen groups.

The obvious goal of a remedial action is to reduce actual or potential human or ecological risk from the contaminants. On a more practical scale, the goal might be merely to treat soil to pass the TCLP test or through the use of containment or isolation actions to prevent further contaminant dispersal if there is no immediate threat to humans or the environment. When soil or water is treated to remove contaminants, the question of how clean it needs to be is often raised. Specifically, how low do the contaminant concentrations have to be before the cleanup is considered successful? The intuitive answer is that the contaminant concentrations should be reduced to background levels or that expected in uncontaminated soil or water. In reality, such concentrations are difficult to obtain. Further, as a remedial process reduces the contaminant concentration in soil or water it becomes more difficult and expensive as the concentration decreases. Eventually, the cost of further efforts must be balanced against the added benefits and the contaminant concentrations will not likely be at background levels before the costs become unreasonable. This has led to greater emphasis on risk and the reduction of risk to an acceptable level rather than focusing on contaminant concentrations alone.

The cost of remediation is an important issue. The Superfund program provided funds for cleanup of NPL sites when no legally responsible and viable parties can be identified. In this case, the taxpayers pay the bill for the cleanup. Often, the cost for cleanup of NPL sites is shared between the state and federal government and the PRPs. For NPL sites on military bases or Department of Energy facilities, those agencies pay for the remediation although it is the taxpayer who ultimately pays the price. Private industry pays for its own sites. Regardless of who pays the bill, excessive costs will be reflected through increased taxes, increased prices, or the poor financial status of private companies. Again, the cost vs. benefits approach must be used. Cost must also be evaluated as various remediation options are considered for a given site. On a more philosophical note, we could consider the effectiveness of money spent on remediation to produce small improvements in risk vs. spending the money addressing other significant social needs with greater potential benefits.

It is difficult to estimate the number of sites that need remediation. The Superfund program maintains the NPL in the United States, with approximately 1200 sites, but there are many sites that are not on the NPL for a number of reasons. For example, it is estimated that approximately 435,000 of 700,000 known underground storage tanks in the United States have leaked. Many of those tanks contained petroleum hydrocarbons of some type. Nearly 1.5 million underground storage tanks have been closed since 1984 in an effort to protect groundwater resources. Worldwide, the magnitude of the problem is much larger.

For organizational purposes it is useful to separate remediation processes according to the general classes of contaminants. The most obvious separation would be inorganic contaminants vs. organic contaminants and that is what is used in this chapter. Inorganic contaminants include metals (see Chapter 9), which cannot be degraded into simple compounds, do not tend to form vapors, and generally do not leach to any great extent. Organic contaminants (see Chapter 10), on the other hand, can be degraded over time to CO₂ and harmless ions by a number of processes. Contaminants may volatilize, and may or may not adsorb strongly to soils or aquifer materials. As will be shown, remediation processes used for one class of compounds may not be appropriate for another. Many

Table 12.1 Soil and Water Remediation Approaches Separated by the Net Effect on the Contaminant

Remediation Technology Effect	Example Technologies			
	Inorganic Contaminants		Organic Contaminants	
	Soil	Water	Soil	Water
Reduce contaminant concentration	Washing, leaching, particle size separation, attenuation, volatilization, phytoextraction, electrokinetics	Reverse osmosis, ion exchange, water softening processes	Washing, leaching, incineration, aeration, bioreactors, land farming, composting, bioaugmentation, indigenous organisms, phytoremediation, soil venting	Filtering, oxidation, aeration, bioaugmentation, phytoremediation, air sparging
Encapsulate contaminant in an inert matrix	Solidification, vitrification	NA	Solidification, vitrification	NA
Reduce contaminant bioavailability without reducing total concentration	Soil amendments, altering redox status	NA	Charcoal additions	NA
Containment	Encapsulation, phytostabilization	Hydraulic containment, slurry walls, sheet piling, grout curtains	Encapsulation, phytostabilization	Hydraulic containment, slurry walls, sheet piling, grout curtains
Removal	Soil excavation	NA	Soil excavation	NA

NA = not appropriate.

sites are contaminated by more than one substance so several approaches may be necessary for remediation. Because organic contaminants have such widely varying properties, the category is often divided into several smaller categories based on volatility, polarity, solubility, or presence of aromatics or halogens. Such a division is beyond the scope of this chapter.

Another useful organizational approach is to consider the net effect of a remedial technology on the contaminant. As shown in Table 12.1, there are five possible effects on the contaminant. The example technologies are described in greater detail in the following sections.

There are innumerable remediation technologies that are in use or have been tested to some degree (see Lehr, 2004). It is simply beyond the scope of this text to present a complete list of options for each contaminant category. An attempt is made to present technologies that have been used or that show promise. In many cases, however, effective remedial technologies have not been identified. The reader is referred to the list of additional resources for a more detailed discussion of the subject.

12.2 INORGANIC CONTAMINANTS

12.2.1 Soil

If we consider the influence of excessive soil concentrations of inorganic contaminants on soil quality, then saline, sodic, and acidified soils would be in need of remediation as well as those soil contaminated by inorganic substances with known harmful effects on various organisms. Generally,

the former categories are not considered under soil remediation and only those elements with known harmful effects on various organisms are considered here. In the context of this text that would include those elements discussed under trace elements, including radionuclides.

Figure 12.2 presents a decision tree for possible remedial action for a site contaminated with inorganic substances. The first decision is whether or not to take action. A decision to take no action can be a conscious one and is often used for sites posing no immediate threat to human health or the environment and for which there is little chance of movement for the contaminants. For both inorganic and organic contaminants, no action may result in *natural attenuation* whereby natural processes act on the contaminants and reduce risk over time. If remedial action is deemed necessary, the next decision is whether the approach will be *in situ* or *ex situ*. Sites that are small and highly contaminated lend themselves to *ex situ* remediation, particularly those involving radionuclides where the half-lives of the isotopes are long. Conversely, large sites having low levels of contamination lend themselves to *in situ* remediation. As compared to sites contaminated with organic chemicals, large sites contaminated with inorganic substances are much more common because of large-scale contamination associated with the mining and smelting of trace elements.

There are six options under *ex situ* remediation with most having a significant engineering component. *Solidification* involves the mixing of solidifying agents with the contaminated soil to produce a concrete-like product with low permeability and with durability under multiple freeze and thaw cycles. Permeabilities can be as low as 10^{-9} cm/s. Solidification reduces TCLP concentrations to acceptable levels and is suitable for stabilizing radioactive waste prior to storage in a nuclear waste repository. A significant disadvantage is that solidification increases waste volume by 10 to 30%. A related process is vitrification, which also creates a product that has low permeability, high durability, and a reduced TCLP concentration. *Vitrification* involves heating the waste to as much as 2000°C to produce a melt that hardens into a glasslike material. One significant advantage to vitrification is that many organic contaminants will also be oxidized during the process, although there may be a need for emission control for waste gases. Volume may be reduced by 25 to 35%. The process is also energy intensive. Both processes encapsulate the contaminant in an inert matrix and have been particularly suited for treating wastes containing radionuclides.

Washing, *leaching*, and *particle-size separation* are all related processes that reduce the contaminant concentration. Washing and leaching employ surfactants, acids, bases, chelators, or

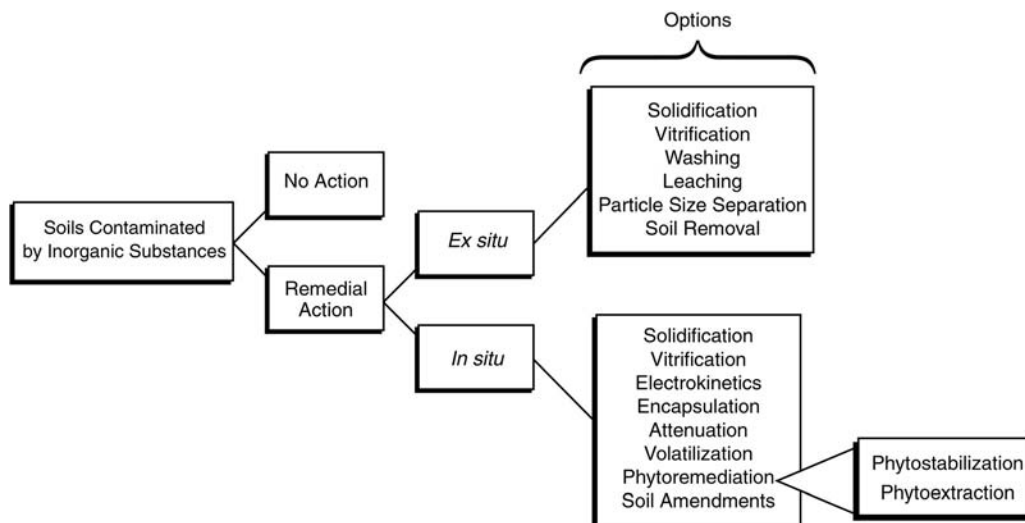


Figure 12.2 Decision tree for soils contaminated with inorganic substances.

ion-exchange resins to remove inorganic contaminants from the soil matrix. Particle-size separation removes the small particles (approximately the clay-sized, or $<2\ \mu\text{m}$, fraction) from the soil matrix and exploits the fact that the concentration of the inorganic substances are generally higher in the finer-sized fractions. Some processes may use both washing and particle-size separation, as shown in Figure 12.3.

Soil removal is a commonly employed technique when contaminated soils are found in residential areas (Figure 12.4). The concept is straightforward in that the contamination is removed and replaced by clean soil. In practice, however, this is a difficult process because of the need to store the excavated material and procure clean replacement soil. Typically, 15 cm of

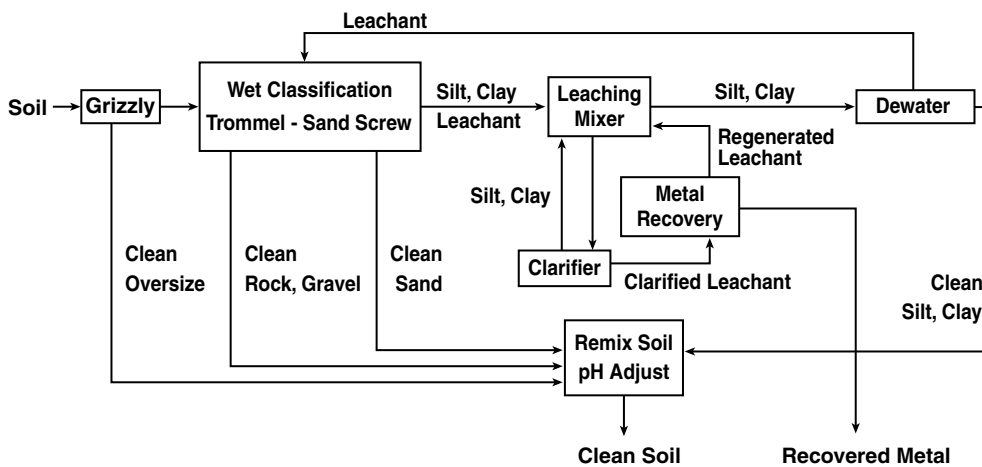


Figure 12.3 Schematic of a soil washing process. (From U.S. EPA, 1992.)



Figure 12.4 Soil excavation from around a home in Joplin, MO. (Photograph credit: Jim Mueller.)

soil is removed and the contaminant levels are checked in the remaining soil. If contaminant levels still exceed the target values, another 15 cm is removed. This process is repeated until up to 60 cm of soil has been removed, depending on the requirements for the site. If contaminant levels still exceed target levels after the maximum allowable depth has been reached, a non-degradable mesh material may be put into place prior to refilling with clean soil. The mesh allows roots and water to pass and acts as a warning to anyone who might dig at the site after the remediation is complete.

Ex situ processes have several disadvantages that bear mentioning. First, conservation of mass still applies and any inorganic substances removed from contaminated soils must still be disposed of or recovered, and this can add substantial cost to the process. Washing, for example, generates large volumes of wastewater that must be treated. A second major disadvantage is that sites contaminated with inorganic substances are frequently large in size. For example, we can estimate that each hectare of land excavated to 60 cm generates approximately 8100 Mg of soil that needs to be treated. Some trace element-contaminated areas exceed 1000 ha in size, so the mass of material quickly becomes overwhelming.

In situ processes (Figure 12.2) have been the focus of increased interest because of the problems outlined above. There are *in situ* versions of solidification and vitrification that produce a similar product as described above; however, the solidified or vitrified monolith is formed in place. This approach is still somewhat experimental but offers the advantage of not having to remove the end products for storage at another location. Electrokinetics is another experimental approach that involves the use of a cathode and an anode placed in the soil. A current is passed between the two electrodes causing the migration of ions toward the electrodes. This is facilitated by the application of fluids that enhance the solubilities of the inorganic contaminants. The end result of the process is the contaminants are contained in a smaller volume of soil, which reduces overall treatment costs.

Encapsulation or capping is a containment strategy that is occasionally used for small sites. The process involves covering the site with a layer of material that has a very low permeability, such as compacted clay or concrete, to minimize percolation of water through the site and to prevent wind-blown dust from the site. This process is analogous to that used for closing landfills. An example from Butte, MT is shown in Figure 12.5. Attenuation simply means dilution of the



Figure 12.5 Encapsulation technology in use in Butte, MT. (Photograph credit: Gary M. Pierzynski.)

contaminated soil with uncontaminated material such as soil, biosolids, or coal fly ash. For contamination that is confined to the soil surface, attenuation can be achieved by mixing with uncontaminated soil that lies beneath the contaminated layer. Volatilization can potentially be used for elements such as arsenic (As), mercury (Hg), or selenium (Se) that can exist in methylated, volatile forms. This is an experimental technique that has shown the greatest promise with Se. Microbes can enhance the formation of volatile dimethylselenide and conditions can be controlled to promote this microbial activity.

Phytoremediation, and the two subcategories of *phytostabilization* and *phytoextraction*, has received considerable attention in recent years. As the name implies, phytoremediation involves the use of plants for remediating a contaminated site. Phytostabilization refers to the use of plants

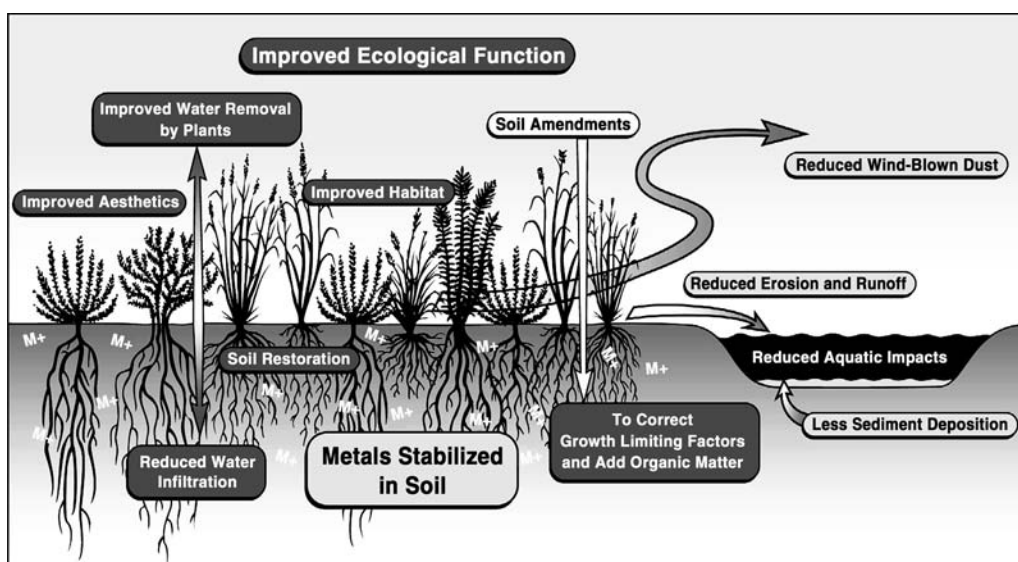


Figure 12.6 In phytostabilization, plants and soil amendments are used to reduce erosion of soil by wind and water, and to reduce metal bioavailability. (From Pierzynski, G. M. et al., *J. Nat. Res. Life Sci. Educ.*, 31, 31–37, 2002. With permission.)

Table 12.2 Influence of Soil Amendments on Subsoil Chemical Properties, Biomass Yield, and Plant Tissue Composition for the Phytostabilization of Pb/Zn Mine Wastes at the Bunker Hill, ID Superfund Site

Treatment	Subsoil Properties		Plant Tissue Composition		
	pH	Extractable Zn (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Yield (Mg/ha)
Control	6.8a ^a	48a	239a	9.7a	<0.1a
Low N biosolids, ash	7.6ab	7.7bc	53b	1.4	1.6b
Low N biosolids, ash, log yard waste	8.0b	3.2c	59b	2.0b	2.4c
High N biosolids, ash	7.6ab	13b	74b	1.7b	3.6d
High N biosolids, ash, log yard waste	8.1b	3.9c	45b	1.4b	4.8d

^a Means with the same letter within a column are not significantly different at $P < 0.05$.

Source: Brown, S. L. et al., *Plant Soil*, 249, 203, 2003.

to vegetate a site and prevent loss of contaminated material through reductions in wind or water erosion. The plants may be grasses, forbs, or trees. Leaching losses may also be reduced because plants reduce net percolation of water through the site due to their transpirational needs. Phytoextraction is an experimental approach that attempts to remove contaminants from soil by plant uptake. Biomass enriched in the contaminants is removed from the site and burned or placed in a repository. The ash contains the contaminants in a much smaller volume and valuable metals can actually be recovered. For high Se biomass, the materials can be processed into animal feed for use in areas that are Se deficient.

Of the two categories of phytoremediation for inorganic contaminants, phytostabilization has gained the greatest acceptance and has been used extensively. The classic example would be a site contaminated by trace elements that has little or no vegetation (see Figure 9.2). Evidence of severe erosion can generally be found at such sites and indications of trace element problems can often be found many miles from the site due to movement and deposition of contaminated sediments by water. There are many possible reasons for the lack of vegetative growth. Trace element phytotoxicities are a problem for elements such as zinc (Zn), copper (Cu), or nickel (Ni). The soils or mine spoil materials may also be poor growth media and are nutrient deficient, have abnormally high or low pH, or have poor soil physical properties. These problems must be corrected before vegetation can be established and maintained over long periods of time.

Figure 12.6 outlines many of the benefits associated with phytostabilization. Reductions in soil erosion improve aquatic habitat because lower amounts of contaminated sediment move off site. Overall, phytostabilization minimizes further dispersal of the contaminants. Aesthetics are improved and over time ecological function is also restored. There has been some debate whether the newly restored areas may serve as an “attractive nuisance” to wildlife that would not otherwise be exposed to the contaminants because they did not frequent the barren areas prior to remediation. Preliminary risk estimates suggest this is not a problem, particularly if soil amendments have reduced contaminant bioavailability.

Various soil amendments have been used to improve the prospects of establishing and maintaining vegetation on contaminated sites. Fertilizers can be used to correct nutrient deficiencies and liming materials can be used to increase soil pH to acceptable levels. Organic by-products such as biosolids or animal manures can add plant nutrients, improve soil physical properties, dilute contaminant concentrations, and can reduce trace element bioavailability to plants, thus decreasing problems with phytotoxicity. Table 12.2 illustrates the effectiveness of various soil amendments on subsoil pH, extractable Zn, biomass production, and plant tissue composition when applied to Pb/Zn mining waste material at the Bunker Hill, ID Superfund site. The increases in subsoil pH and subsequent decrease in Zn phytoavailability (as indicated by extractable Zn levels), coupled with the addition of plant nutrients, allowed vegetation to be successfully established on this barren area. Here the soil Zn bioavailability has been reduced without changing the total Zn concentration in the soil.

The concept of phytoextraction was developed from observations by botanists that certain plant species, called *hyperaccumulators*, had very high concentrations of selected elements. Hyperaccumulators have been found for As, cobalt (Co), Cu, Ni, Pb, Se, uranium (U), and Zn. A plant tissue concentration of 1000 mg/kg would be indicative of hyperaccumulation for all but Se and Zn, where concentrations as high as 10,000 mg/kg are possible. Figure 12.7 illustrates the two different approaches to phytoextraction. Natural hyperaccumulation uses native hyperaccumulating plant species that can be managed to reduce metal concentrations in soils. Induced hyperaccumulation uses plants that do not normally take up large amounts of metals, but can be induced to do so by the addition of conditioning fluids that increase metal solubility and uptake by plants.

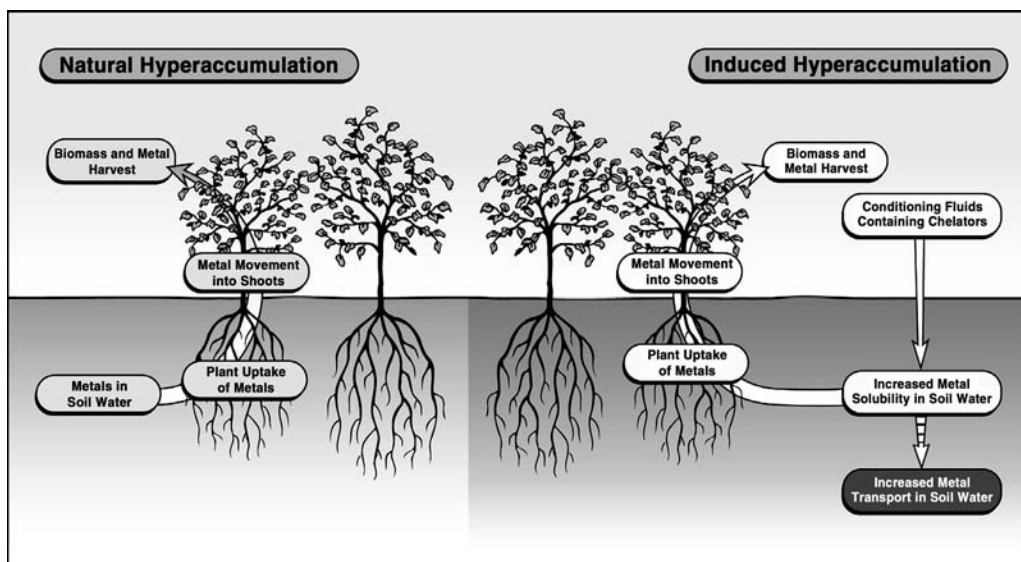


Figure 12.7 In phytoremediation, metals move into the plant biomass and the biomass is harvested. (From Pierzynski, G. M. et al., *J. Nat. Resour. Life Sci. Educ.*, 31, 31–37, 2002. With permission.)

Example Problem 12.1

The ability of a given plant species to remove an element from the soil would be a product of the biomass produced and the concentration of that element in the biomass, as shown below:

$$\frac{1000 \text{ mg Ni}}{\text{kg biomass}} \times \frac{2000 \text{ kg biomass}}{\text{ha yr}} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = \frac{2.0 \text{ kg Ni removed}}{\text{ha yr}}$$

We can calculate the approximate mass of an element present in 1 ha of soil using a depth, bulk density, and the soil contaminant concentration. We can then estimate the number of harvests required to remove a given amount of an element from that hectare. For example, assuming a bulk density of 1.35 g/cm^3 we have:

$$\frac{135,000 \text{ kg soil}}{\text{ha cm}} \times 30 \text{ cm} \times \frac{100 \text{ mg Ni}}{\text{kg soil}} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = \frac{405 \text{ kg Ni}}{\text{ha}}$$

which would require 203 years to remove at $2.0 \text{ kg Ni/ha/year}$.

The example problem illustrates one of the disadvantages to using this approach: low removal rates. This is a result of low contaminant concentrations in the biomass or low biomass production. Overall, the hyperaccumulators do not produce large quantities of biomass. One long-range solution to this problem is to use plant breeding or biotechnology to develop plants that hyperaccumulate and produce more biomass. Another experimental solution is to use plants that produce high quantities of biomass but do not hyperaccumulate the inorganic contaminant. Liquids containing chelating agents that solubilize metals in soils are added to the soil while the plants are actively growing, causing increased plant uptake. The high metal concentrations in the plant induce a phytotoxic response but that is not a concern because the crop is harvested shortly afterward anyway. Significant concerns exist regarding the increased potential to leach metals from the soil with this

Table 12.3 Influence of Dietary Pb on Relative Bioavailability of Pb Based on Blood, Kidney, Liver, and Bone of Rats

Treatment	Blood	Kidney	Liver	Bone
Pb acetate	100a ^a	100a	100a	100a
Pb-contaminated soil	34b	48b	27b	34b
Pb-contaminated soil + P	33c	36c	21c	22c

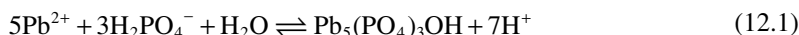
Note: Lead sources include Pb acetate, Pb-contaminated soil, and Pb-contaminated soil amended with P. Bioavailability is relative to Pb acetate, a highly soluble form of Pb that is readily absorbed by the animals.

^a Means with the same letter within a column are not significantly different at $P < 0.05$.

Source: Hettiarachchi, G. M. et al., *J. Environ. Qual.*, 32, 1335, 2003.

approach. To date, there have been no large-scale remediation efforts performed with phytoextraction, although it remains an area of active research.

Soil amendments are often used as part of phytostabilization efforts, as described above, but can also be the primary method of remediation themselves. One example that is discussed in Chapters 9 and 13 is the use of P amendment for Pb-contaminated soil. The proposed mechanism is the formation of insoluble Pb phosphates in the soil, as shown below:



Because ingestion of Pb-contaminated soil is one of the primary routes of exposure for humans, these Pb phosphates must be so insoluble that they do not dissolve in the digestive system and pass through without being absorbed into the body (i.e., having a low bioavailability).

An example of the effect of P addition on Pb-contaminated soil is shown in Table 12.3. Here rats were given Pb as a soluble salt (Pb acetate), Pb-contaminated soil, or Pb-contaminated soil amended with P. The data clearly show the relative bioavailability of Pb is higher when Pb is given as a soluble salt as compared to equivalent doses of Pb from soil. Moreover, the addition of P to the soil reduces Pb bioavailability compared to soil without P amendment.

There are many other soil amendments studied that may reduce the bioavailability of inorganic contaminants to plants, animals, or humans. These include liming materials, iron (Fe), manganese (Mn), and aluminum (Al) (oxy)hydroxides, zeolites, clays, ferrous sulfate, various composts, and alkaline biosolids. The obvious advantage for remediation is that soil amendments are relatively easy to add to soil *in situ*, even over large areas. It is likely that the use of soil amendments will become increasingly popular as part of remedial activities.

12.2.2 Water

For many of the inorganic contaminants, particularly the cationic metals and some oxyanions, movement through soil is restricted and large-scale contamination of groundwater is not common. There are instances where shallow aquifers actually intersect existing or previous mining activities and significant contamination of groundwater occurred. Similarly, in watersheds where vegetative cover is limited, there may be significant movement of inorganic contaminants to surface waters. Often aquatic life criteria are exceeded in such surface waters, but remediation generally involves processes described above for soils to limit movement of inorganic contaminants and no direct remediation of water is performed. If either surface water or groundwater is used for drinking water purposes, some remedial action may be necessary.

The remedial alternative used most often for water contaminated with inorganic substances is abandonment of the source. If private wells are supplying drinking water to homes, then the installation of a public water system can solve the problem. Alternatively, bottled water may be

used for cooking and direct consumption. If a public water system has difficulty meeting drinking water standards, new wells may have to be drilled outside of the contaminated areas or new surface water sources may need to be located. Dilution of contaminated water with clean water will also allow the finished water to meet standards.

Large-scale purification systems are generally not practical for public water systems. Water softening processes may reduce the concentrations of inorganic contaminants somewhat in the finished water. Purification systems for individual homes are quite effective and have been used in many remedial actions. Water softeners or conditioners for individual homes, reverse osmosis systems, ion-exchange columns, and distillation may reduce contaminant concentrations to acceptable levels. The difficulty with this approach for a remedial action is that the systems require regular maintenance to remain effective. It is difficult to ensure that all of the required maintenance is performed, even if that maintenance is provided at no cost.

12.3 ORGANIC CONTAMINANTS

Many of the remediation options that were described for inorganic contaminants would also be appropriate for organic chemicals. However, organic contaminants have several characteristics that make additional remediation options available. Two such characteristics are biodegradability and volatility. Biodegradability presents opportunities for degradation of organic contaminants through biological activity, usually by microorganisms or possibly by plants. Volatilization exploits the high vapor pressure of some compounds and allows the removal of organic contaminants from soil or water as vapors. The term *volatile organic chemicals* (VOCs) is often used to describe this group of organic contaminants. There are other subcategories of organic chemicals that are often used. These are grouped together because of similar chemical properties or because the collection of organic chemicals often occurs together as contaminants. Examples include PAHs (polycyclic aromatic hydrocarbons), BTEX (for benzene, toluene, ethylbenzene, and the xylenes), and PCBs (polychlorinated biphenyls).

Several key properties of organic chemicals are important in their fate and transport in the environment (see Chapter 10) as well as in the approach used for remediation, regardless of whether the contamination is with soil or water. Biodegradability, polarity, solubility, volatility, and the tendency to adsorb to soil or aquifer materials all need to be considered for remediation. Some compounds lend themselves to biodegradation while others, particularly halogenated or aromatic substance, can be quite resistant to biodegradation. Polarity and solubility are closely related in that polar substances tend to have high solubilities, and vice versa. Highly soluble substances can be more mobile in soil and can also be more accessible to microorganisms for biodegradation. The tendency to adsorb to soil or aquifer materials also greatly influences mobility and accessibility for microorganisms. This characteristic is also related to polarity. Nonpolar substances generally have a high affinity for the naturally occurring organic C in soils and are strongly adsorbed.

Soils and water contaminated with organic substances often involve more than one compound. Therefore, more than one remediation method may be necessary to address all of the contamination.

12.3.1 Soil

Figure 12.8 presents the decision tree for soils contaminated with organic substances. As with the inorganic contaminants, no action can be a conscious decision. If remedial action is to be undertaken, there are *ex situ* and *in situ* options. Solidification, vitrification, washing, leaching, soil removal, and encapsulation for both *ex situ* and *in situ* approaches are similar to that described for the inorganic contaminants.

The remaining *ex situ* options include incineration, aeration, and bioremediation, all of which attempt to reduce the concentration of the contaminant. Incineration is similar to vitrification in

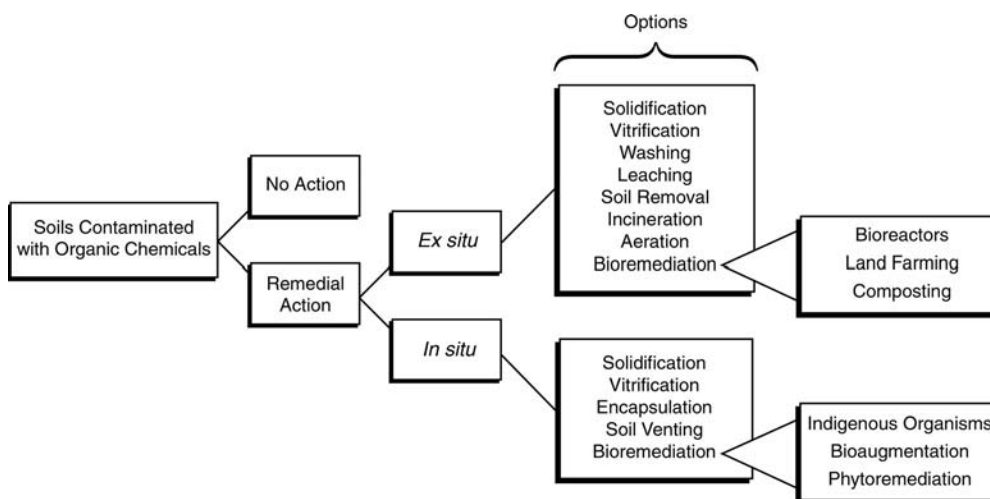


Figure 12.8 Decision tree for soils contaminated by organic chemicals.

that the soil is heated, but incineration is performed with the specific objective of oxidizing the organic chemicals, preferably all the way to CO_2 and H_2O . This approach has been used for soils contaminated with highly toxic organic chemicals such as dioxins. Aeration is used for VOCs and can be performed many different ways. Aeration can be passive, as is often used with soils contaminated with gasoline around a leaking underground storage tank. In this situation the tank is removed and the soil is simply exposed to the atmosphere until most of the VOCs have evaporated. Aeration can also be accomplished by forcing air through a volume of soil or providing a suction that concentrates the organic chemicals to facilitate the removal of VOCs.

Bioremediation takes advantage of the ability of organisms to degrade organic chemicals into simpler and, it is hoped, less toxic substances. Generally this is accomplished with microorganisms, although plants have some ability to metabolize organic contaminants. Microorganisms may use the organic compounds as a source of food, because they contain C, or they may co-metabolize the organic contaminants. Co-metabolism means that the organisms convert the organic compounds to other substances as a by-product of their normal biochemical processes and do not necessarily use the contaminants as a source of energy.

There are many types of microorganisms. For bioremediation under aerobic conditions, the bacteria and, to a lesser extent, fungi play the largest role in degradation of organic substances. Under anaerobic conditions the role is almost entirely filled by bacteria. Of particular importance is that an organism or consortium of organisms exists that can degrade the organic substance or substances in question. If a soil is contaminated by an organic chemical, the process of natural selection may result in a species or group of species with an enhanced ability to degrade that organic chemical. Experimentally, genetically engineered microorganisms (GEMs) have been developed for the specific purpose of bioremediation. Ideally, we could inoculate the soil with these organisms to facilitate degradation. Because bioremediation requires active growth of microorganisms, it follows that the basic needs of the organisms must be met in order for degradation of organic contaminants to take place as rapidly as possible. This includes appropriate temperature, moisture, pH, nutrient, and redox conditions as well as a usable source of energy.

The use of bioreactors is one way to ensure that optimal growing conditions are maintained during bioremediation. *Bioreactors* are enclosed vessels into which contaminated soil is placed and microbial growth is promoted for the purpose of bioremediation. Often the soil is kept as a slurry. Nutrient solutions can easily be added, and temperature and aeration are easily controlled. Once

the desired reduction in contaminant concentrations has been attained, a new batch of soil is introduced into the vessel.

Land farming is a method often used for organic substances such as pesticides that are normally released into the environment in small amounts. If soil has become highly contaminated with a pesticide, say, from a spill, the soil is spread over land such that the amount of the pesticide applied is within the normal application rates for that pesticide (Figure 12.9). The fate and transport would then be the same as an application of that pesticide according to the label.

Composting can also be used for soils contaminated by organic chemicals. The soil alone will not compost but will when mixed with compostable organic wastes such as grass, leaves, manures, or biosolids. The composting process involves a period of high microbial activity that generates heat and stabilizes the organic C in the material. This high microbial activity can help to degrade certain organic substances.

Soil venting and bioremediation are the remaining choices for *in situ* remediation that have not yet been described. Soil venting (also called vapor extraction) is similar to *ex situ* aeration except that the soil is not removed and a means of forcing air into or a means of applying a vacuum to a volume of soil must be devised. Generally this involves inserting screened or slotted pipes into the contaminated soil. This method works for VOCs and sometimes requires that the waste gases be captured and treated or burned, particularly when the remediation is taking place in a residential area.

In situ bioremediation can be approached three different ways: use of indigenous soil microorganisms, *bioaugmentation*, and *phytoremediation*. Degradation of some organic contaminants will proceed by the action of indigenous soil microorganisms; sometimes this process can be hastened by supplementation with nutrients or water to ensure active microbial growth over extended periods of time. Bioaugmentation refers to the inoculation of soil using microorganisms with an enhanced ability to degrade the organic contaminant. As described above, these organisms can be isolated from native populations or be genetically engineered. Once an organism with the desired capabilities has been isolated, the population can be increased so that an inoculum can be prepared for use. Unfortunately, applications of bioaugmentation have had limited success. Generally, when the organisms are placed in their new environment, they tend to die off within a few weeks. The reasons for this are not clear. It may be related to their adaptability to site conditions or to some poorly understood microbial ecology issues.

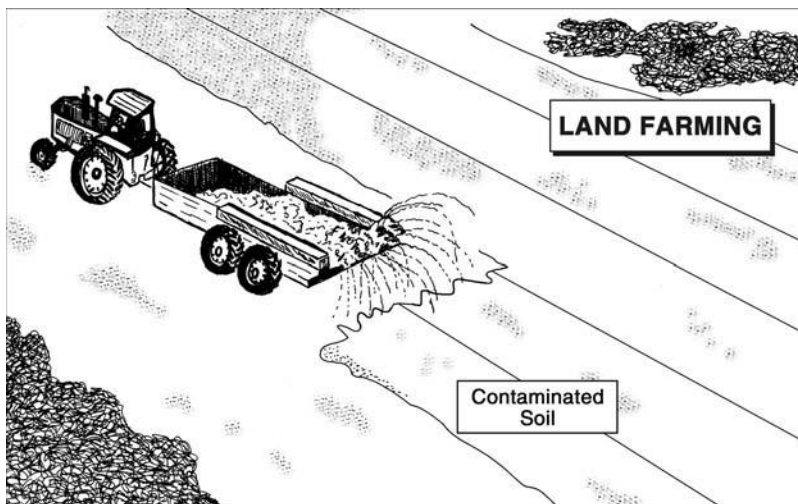


Figure 12.9 Land farming as a bioremediation option for soils contaminated by organic chemicals.

In situ phytoremediation for organic contaminants is quite different from phytoremediation for inorganic substances. Both involve the use of plants for remediation, but the mechanisms are not the same. Phytoremediation of organic chemicals involves promoting plant growth on contaminated sites with the goal of reducing the contaminant concentration in the soil (see Environmental Quality Issues/Events at the end of this chapter). There are several ways in which the plants accomplish this task. The most important mechanism is likely related to the influence of plant roots on soil microbial activity. There is a small volume of soil surrounding each root that has enhanced microbial activity compared to the bulk soil. This zone is called the *rhizosphere*, or the volume of soil directly influenced by growing plants. The roots exude C-containing materials that the microbes use as sources of energy. In addition, the roots draw water and some nutrients and contaminants toward them. Thus, the rhizosphere is a more favorable environment for microbial growth than the bulk soil and this enhanced microbial activity is thought to hasten the degradation of organic contaminants. The plants themselves can also metabolize some organic contaminants and some VOCs can be moved from the soil to the atmosphere via transpiration.

12.3.2 Water

Groundwater contaminated by organic chemicals is a serious problem for a number of reasons. The number of sites with known or potential groundwater contamination is large considering the number of NPL sites and the estimated number of leaking underground storage tanks. Once contamination has occurred, it is very difficult to remediate because the contaminated materials may lie a considerable distance below the surface, contaminated groundwater cannot easily be isolated, the contaminant also interacts with the aquifer material, there may be contaminant present in the unsaturated zone that has not yet reached the groundwater, and the groundwater is moving, albeit slowly. If we consider the volume of water that can be contaminated by a relatively small volume of an organic chemical, it seems necessary to clean up contaminated sites because a very important resource is at risk.

Example Problem 12.2

One 208 L drum (55 gallons) of trichloroethylene (TCE, the most prevalent organic contaminant at Superfund sites) could raise the TCE concentration of 60×10^9 L (16×10^9 gallons) of water from 0 to 5 $\mu\text{g/L}$, the MCL for TCE in drinking water. This is calculated as follows:

The density of TCE is 1.46 kg/L so 208 L has a mass of

$$208 \text{ L} \times \frac{1.46 \text{ kg}}{\text{L}} = 303.7 \text{ kg}$$

$$\text{Contaminated volume} = 303.7 \text{ kg TCE} \times \frac{10^9 \mu\text{g}}{\text{kg}} \times \frac{\text{L}}{5 \mu\text{g}} = 60.7 \times 10^9 \text{ L}$$

If a site is found to have groundwater contaminated with organic chemicals, there are several important pieces of information that are needed to determine the urgency and overall approach to the remediation. As with soil remediation, the identity and chemical properties of the organic chemicals are important, i.e., the density and solubility of the chemical. For those organic chemicals that are immiscible in water and less dense than water we would expect the contaminant plume to remain at the top of the aquifer. Conversely, those chemicals immiscible in water and with a density greater than water will attempt to sink to the bottom of the aquifer. Organic chemicals with a high solubility

will likely be dispersed throughout the aquifer. The direction and approximate velocity of groundwater flow are also needed. Obviously the contaminant plume will follow the direction of flow and the aquifer velocity may provide an estimate of how far the plume has traveled. This is particularly important if there are wells nearby using water from the aquifer. Fortunately, groundwater does not move quickly unless there is karst geology. The average pore-water velocity (also known as average linear velocity or seepage velocity) for water in an aquifer can be estimated with

$$v = \frac{K}{\Phi} \times \frac{\Delta h}{\Delta l} \quad (12.2)$$

where v = velocity (cm/s), K = saturated hydraulic conductivity (cm/s), Φ = volumetric porosity (unit less), and $\Delta h/\Delta l$ = hydraulic gradient (unit less). The saturated hydraulic conductivity is a property of the aquifer and characterizes the ease at which water moves through the material. Gravel would have a much higher K value than clay. The hydraulic gradient is the change in elevation at the top of the water table (Δh), relative to some reference value, across a given distance (Δl). As the hydraulic gradient increases, v also increases. The potential interaction between the contaminant and the aquifer material may also be considered. If the contaminant adsorbs to the aquifer material, the velocity will be less than that of the water. Often we are interested in how long it will take a contaminant to move from a given point to the nearest well using water from the aquifer. These calculations are generally performed as a worst-case scenario assuming no interaction between the contaminant and the aquifer material and, if ranges of values are given for K , the maximum value is used.

Example Problem 12.3

Calculate the length of time required for a contaminant to move 2 km in groundwater when K is estimated to range from 10^{-4} to 10^{-6} cm/s, $\phi = 0.30$, and the hydraulic gradient is 0.14:

$$\text{Time} = 2 \text{ km} \times \frac{10^5 \text{ cm}}{\text{km}} \times \frac{0.30}{0.14 \times 10^{-4} \text{ cm/s}} \times \frac{1 \text{ yr}}{31.536 \times 10^6 \text{ s}} = 136 \text{ yr}$$

or we can calculate the distance moved in 1 year:

$$\text{Distance} = 0.14 \times \frac{10^{-4} \text{ cm/s}}{0.30} \times \frac{31.536 \times 10^6 \text{ s}}{\text{yr}} = \frac{1472 \text{ cm}}{\text{yr}}$$

or about 48.3 ft in 1 year or 10^{-6} miles per hour.

These examples illustrate that under many conditions groundwater does not move very fast and there is little need to rush into remedial action. There is adequate time for careful planning.

Figure 12.10 represents the decision tree for groundwater contaminated by organic chemicals. As before, no action can be a deliberate decision. If a contaminant plume is small and there are no wells nearby, then a decision to wait may be allowed. With the speed at which remediation technologies are being developed or improved, we could certainly make a case for waiting for a more effective or less expensive alternative to be adopted.

Containment is used for small contaminant plumes and can be either hydraulic or physical barriers. A hydraulic barrier uses injection wells downgradient from the contaminant plume to reduce the hydraulic gradient across the site to very low values. The net effect is to reduce the groundwater velocity to near zero, thus containing the contaminants. This can be used as a temporary

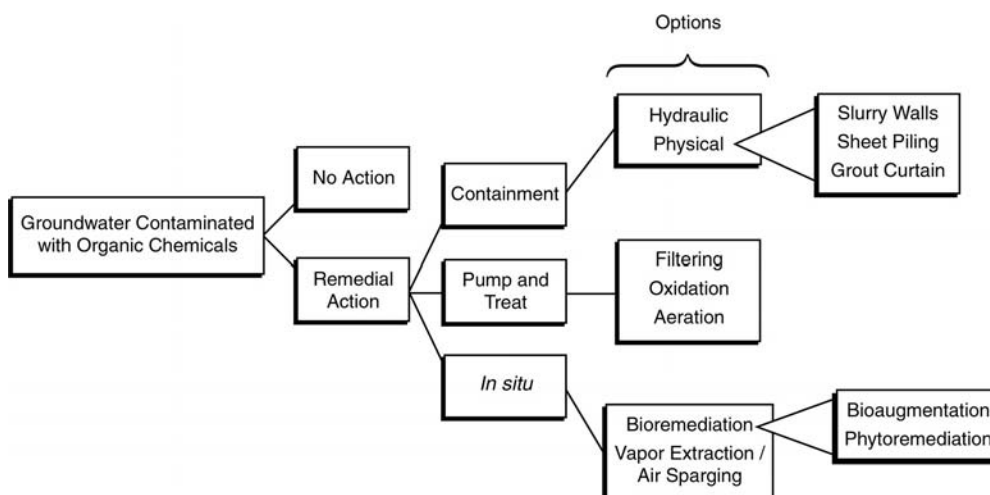


Figure 12.10 Decision tree for groundwater contaminated by organic chemicals.

measure until other alternatives are put into place. The goal of physical containment measures is the same except that the barriers are made of solid materials that must be installed. Slurry walls consist of trenches filled with clay mixtures that have a very low permeability (or saturated hydraulic conductivity). Sheet piling is generally made of steel sheets that are driven into the ground and grout curtains are installed like slurry walls except the grouting material hardens. Physical barriers are prone to leaking, are difficult to install and maintain, and are poor long-term solutions to groundwater contamination.

Pump-and-treat methods are among the most popular groundwater remediation methods used. The basic process is that a well or a number of wells are placed into or near the contaminant plume. Water is pumped from these wells and treated with a variety of processes to reduce the contaminant concentration. The treated water is often injected back into the aquifer upgradient from the plume to help force the contaminant to the extraction wells or downgradient from the plume to help form a hydraulic barrier to help contain the plume. The treatment processes can include filtering, oxidation, or aeration. Filtering can be through charcoal or biofilters. Oxidation of organic chemicals can be promoted by the addition of oxygen gas or hydrogen peroxide, or with ultraviolet light. Aeration works well for VOCs and can simply involve allowing the water to fall through an aeration tower. Figure 12.11 shows a schematic of a pump-and-treat process where treated water is injected into the aquifer both up- and downgradient from the contaminant plume. Both injection wells help force the contaminants to the extraction well.

In situ remediation of groundwater would be the most desirable way to address contaminated groundwater, but is one of the most technically challenging approaches. Bioremediation can be either as bioaugmentation or phytoremediation. Bioaugmentation involves injecting microorganisms into the aquifer in an attempt to induce microbial breakdown of the contaminants. Unfortunately, aquifers are generally cold and have limited nutrients, oxygen, and C compounds to act as energy sources. Even when the missing ingredients are added, the microorganisms have difficulty surviving and performing the desired function. Phytoremediation has been used successfully when groundwater is close to the surface and the contaminant concentrations are not too high. This generally involves using deep-rooted trees that thrive in wet environments, such as poplars, cottonwoods, or willows. The environment is often adjacent to streams, rivers, or lakes with the groundwater flowing toward the body of water. The tree roots intercept some of the water and use it for transpiration. In the process they can degrade or volatilize some of the contaminants.

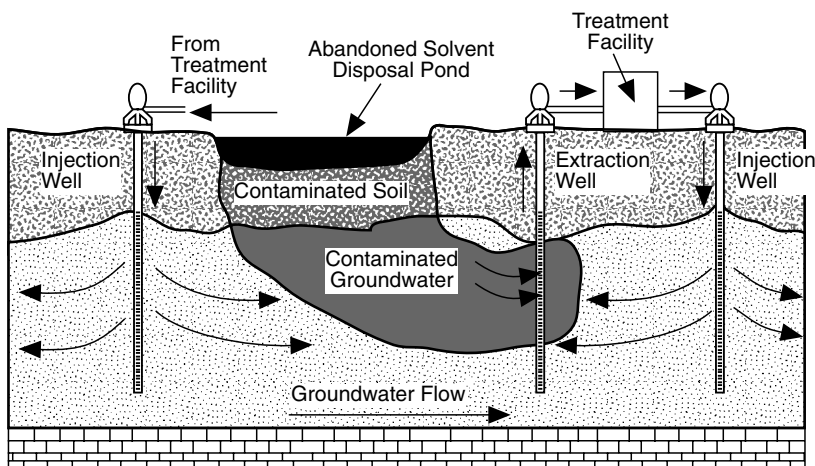


Figure 12.11 Schematic of well placement for a pump-and-treat process for groundwater contaminated by leachate from an abandoned solvent disposal pond. (Drawing by Sarah Blair.)

Vapor extraction/air sparging involves forcing air into an aquifer or using vapor extraction wells under a vacuum, or a combination of both, to try to get VOCs out of the water, aquifer material, and vadose zone. The captured vapors can be treated with biofiltration, adsorption onto charcoal, or combustion.

A significant limitation of the pump-and-treat methods and the *in situ* approach is the difficulty in getting contaminant concentrations down to low levels. Typically, as a remediation process begins, the contaminant concentrations in the water decrease rapidly but eventually level off and will not go lower without significant additional effort. If this plateau in concentration is not as low as needed, the remediation may not be considered successful.

Environmental Quality Issues/Events

Phytoremediation of Petroleum-Contaminated Soils: Case Study

The extraction, processing, and use of crude oil and its refined products present many opportunities for soil contamination. Crude oil spills occur at well sites; near pipelines and storage facilities; during transport by rail, truck, or ship; and at refinery facilities. Similar opportunities exist for accidental release of refined products such as gasoline, diesel, or jet fuels. In addition, these materials are often stored in underground storage tanks that may leak and contaminate the underlying soil. Recent EPA regulations on underground storage tanks have greatly reduced the chances of leaks from tanks located on commercial properties, but many existing storage sites already had soil contaminated with petroleum products.

The chemical identity of the contaminants depends on the type of petroleum product. Crude oil is a complex mixture of thousands of hydrocarbons that can be divided into three general classes consisting of saturated hydrocarbons, aromatic hydrocarbons, and polar organic compounds. Similarly, refined products such as gasoline have hundreds to thousands of hydrocarbon compounds. Some of the major constituents in gasoline are *n*-butane, *n*-pentane, isopentane, benzene, toluene, ethylbenzene, and the xylenes. The term petroleum hydrocarbons (TPH) is often used to describe a wide range of petroleum hydrocarbon constituents measurable by a particular type of analysis. When dealing with petroleum-contaminated soils, we can measure the concentration of individual petroleum constituents or the TPH concentration. Many of the petroleum constituents are toxic or carcinogenic for humans and other organisms. The TPH concentration has little to do with risk, but can be used as an indicator of the degree of contamination and the success of a remediation process.

Table 12.4 Phytoremediation of Petroleum-Contaminated Soils from the Craney Island Fuel Facility, Norfolk, VA

Treatment	% Petroleum Degradation			
	6 months	12 months	18 months	24 months
Unvegetated	12a*	21b	17b	31c
Clover	11a	29ab	34a	50a
Fescue	9a	33a	34a	45ab
Bermuda	13a	27ab	30ab	40b

* Means followed by the same letter in a column are not significantly different using LSD at $P < 0.05$.

Phytoremediation, as a type of bioremediation, is a promising approach for remediation of soil contaminated with petroleum hydrocarbons. Many of the less complex constituents of petroleum products readily undergo bioremediation by soil microorganisms in unvegetated soil. However, there is a significant recalcitrant fraction that is very slow to degrade. The TPH concentrations may decline rapidly for a short time after a petroleum spill occurs, but eventually will reach a level from which further decreases are unlikely or will be very slow. At this point, the use of plants may help reduce TPH concentrations further. Some of the advantages of phytoremediation are that it may be performed without disturbing the soil, it can be less expensive than the alternatives, it is powered by solar energy, and it has the potential to attain lower contaminant concentrations than other remediation options.

The mechanism by which plants facilitate the degradation of petroleum hydrocarbons in soils is not clearly understood. As discussed in the text, there are several possible mechanisms. Contaminant reduction may be due to enhanced growth of microorganisms in the rhizosphere, co-metabolism of the contaminants by the plants, or the loss of volatile compounds via transpiration. Microbial densities in the rhizosphere can be ten times higher than in unvegetated soil. In the case of TPH, co-metabolism and volatile losses are not likely and microbial degradation in the rhizosphere most probably is the mechanism by which petroleum compounds are degraded.

Phytoremediation of soils contaminated with petroleum hydrocarbons has been attempted at several locations. Data from one such site are presented in Table 12.4. The soil from this site was contaminated with diesel fuel and had been placed in a bioremediation cell. The soil came from a refueling facility for ships located on Craney Island near Norfolk, VA, one of the largest such facilities operated by the U.S. Navy. The bioremediation cell was 0.2 ha in size and was equipped with a leachate collection system. There was a 45 cm layer of contaminated soil placed on top of 90 cm of sand. The plots were established in the soil layer and consisted of four treatments with six replications. The treatments consisted of an unvegetated control and plots vegetated with tall fescue (*Festuca arundinaceae*), white clover (*Trifolium repens*), or bermudagrass (*Cynodon dactylon*).

There was some degradation of TPH in the unvegetated treatment over time (Table 12.4). After 6 months there was no significant difference in TPH concentration between treatments, but this was not unexpected because the plants were relatively small and the root systems were not well established. After 12 months, the fescue treatment resulted in significantly higher degradation compared to the other treatments, and by 24 months all vegetated treatments had significantly higher degradation compared to the unvegetated treatment. With further development it is likely that phytoremediation of petroleum-contaminated soils can be a viable and less costly option, both *in situ* and *ex situ*, compared to currently accepted practices. Current estimates indicate that phytoremediation is two to three times less expensive than bioremediation without plants and ten times less expensive than placing the soil in a landfill.

(Special thanks to A. Paul Schwab, Purdue University, for supplying the information for this case study. The research was funded by the U.S. Department of Defense's Advanced Applied Technology Demonstration Facility (AATDF) housed at Rice University and was conducted in conjunction with industrial cooperators.)

PROBLEMS

- 12.1 A Zn hyperaccumulator plant has a Zn concentration of 6000 mg/kg and produces 4000 kg biomass/year. Calculate the annual Zn removal rate for the plant species.
- 12.2 A contaminated site has 500 mg Cu/kg in the upper 30 cm of soil. Calculate the required annual removal rate for Cu if you wanted to use phytoextraction on this site and complete the remediation in 20 years. Assume a soil bulk density of 1.35 g/cm³. If a Cu hyperaccumulator had 1000 mg/kg Cu in the tissue, how much biomass would need to be produced each year to complete the remediation in 20 years.
- 12.3 Discuss advantages and disadvantages of *in situ* vs. *ex situ* remediation.
- 12.4 Describe the various manifestations of phytoremediation. How do they differ for inorganic vs. organic contaminants?
- 12.5 Describe the various manifestations of bioremediation. What are some of the limitations and challenges of this approach?
- 12.6 The density of vinyl chloride (C₂H₃Cl) is 0.91 kg/L and the MCL for drinking water is 2 µg/L. Calculate the volume of water that could be contaminated by 1 L of vinyl chloride if the concentration of vinyl chloride in the water was raised from 0 to 2 µg/L. Repeat the calculation for ethylbenzene (C₈H₁₀) with a density of 0.87 kg/L and a MCL of 70 µg/L.
- 12.7 The density of carbon tetrachloride (CCl₄) is 1.59 kg/L and the MCL for drinking water is 5 µg/L. Calculate the volume of carbon tetrachloride required to raise the carbon tetrachloride concentration of 1 L of water by 5 µg/L.
- 12.8 An aquifer has a hydraulic conductivity of 10⁻⁵ cm/s, a porosity of 0.35, and a hydraulic gradient of 0.05. Calculate the length of time (in years) required for groundwater to move 1 km.
- 12.9 An aquifer has a hydraulic conductivity of 10^{-3.5} cm/s, a porosity of 0.40, and a hydraulic gradient of 0.019. Calculate the average pore-water velocity in cm/s and miles per hour. Determine how far the groundwater travels in 1 year (in cm/year).
- 12.10 Calculate the mass of soil in the bioremediation cell described in the case study assuming a bulk density of 1.20 g/cm³. Calculate the cost of remediating the soil with phytoremediation at \$15/Mg (metric ton or 1000 kg), with bioremediation at \$45/Mg, and with land filling at \$150/Mg.
- 12.11 The U.S. EPA provides information on contaminated sites on the National Priorities List. Visit the Web site at <http://www.epa.gov/superfund/npl.npl.htm> and identify an NPL site of interest to you. In one or two paragraphs, provide a description of the site, threats and contaminants, cleanup approach, and current status of the site in the Superfund process.

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Risk Assessment

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13.1 INTRODUCTION

Risk is defined as the probability or chance of injury, loss, or damage. This is a very general definition of risk that includes situations such as financial losses, storm damage, and human or animal health effects from exposure to pollutants. This chapter summarizes the basic concepts used in risk assessment and illustrates how the risk assessment process is used in writing environmental regulations or determining cleanup levels for contaminated sites with an emphasis on soils and waters. There are two major reasons we would be concerned with risk assessment for soil contaminants. First, if the concentration of a substance in soil is deliberately increased, will any organism experience an unacceptable increase in risk? Second, what increased risks are realized by organisms because of soil contamination that has already occurred? Recall from Figure 1.2 that there are both direct and indirect ways for organisms to be exposed to substances in soils that can cause harm. Therefore, an increase in risk can be realized from the ingestion of soil itself (e.g., by children or grazing livestock) or indirectly from the consumption of groundwater or surface water contaminated by a substance present in soil, or from the consumption of crops grown in, or livestock exposed to, the contaminated soil.

Our definition of risk includes effects on any organism, although the tendency is to focus the discussion on human health effects. Morbidity and mortality, both immediate and delayed, are the two general effects of concern. More is known about human risk assessment because of our strong interest in protecting human health. In recent years there has been increased interest in ecological

risk assessment. For our purposes, ecological risk assessment addresses the effects of contaminants on all organisms besides humans. Most of the discussion in this chapter considers human and ecological risks together. Special consideration is given to ecological risk in a separate section at the end of this chapter.

Risk can be quantified as the number of negative outcomes (injury, loss, or damage) divided by the number of organisms exposed to the risk, or by some other measure of exposure to the risk (e.g., miles driven). Some risks are very easy to quantify. For example, the risk of death or injury in an automobile accident is relatively easy to determine. The negative outcome is generally immediate, the cause is not in question, and the exposed population is also relatively easy to identify. It is reasonable to assume all people are exposed to this risk since nearly everyone drives or rides in automobiles. Other risks are much more difficult to quantify because neither the negative outcome nor the exposed population is easy to identify and quantify. Exposure to potentially carcinogenic substances would be a good example. The negative outcome may not occur for many years after exposure and, generally, all cases of a given type of cancer cannot be related to a single causative factor.

Table 13.1 provides risk information for a number of causes of death for all age groups in the United States. For the ten leading causes of death, the annual individual risk was calculated by dividing the number of deaths for each cause in 2000 by the U.S. population at that time (approximately 281,000,000). This assumes the entire population is exposed to each risk which, of course, is not always true. The exposed population is usually a subset of the total population. Not everyone drives or rides in automobiles and even fewer travel by commercial aviation, and these individuals are not exposed to those risks. The assumption is more valid for causes such as unintentional

Table 13.1 Individual Risk from Various Causes of Death in the United States

Cause of Death	Annual Individual Risk	Ratio ^a
Ten Leading Causes of Death^b		
Heart disease	2.8×10^{-3}	357
Cancer	2.1×10^{-3}	476
Cerebrovascular	6.0×10^{-4}	1,667
Bronchitis, emphysema, asthma	3.9×10^{-4}	2,564
Accidents and injuries	3.5×10^{-4}	2,857
Pneumonia and influenza	3.2×10^{-4}	3,125
Diabetes	2.3×10^{-4}	4,348
HIV	1.6×10^{-4}	6,250
Suicide	1.2×10^{-4}	8,333
Liver disease	9.6×10^{-5}	10,417
Other Causes of Death		
Motor vehicle accidents	1.6×10^{-4}	6,250
General aviation ^c	2.9×10^{-6}	344,800
Commercial aviation ^c	5×10^{-7}	2,000,000
Lightning	3.7×10^{-7}	2,702,000

^a One death per number of people in population.

^b Based on 1995 data.

^c For the 10-year period ending in 1997.

Source: Data from the Centers for Disease Control and National Transportation Safety Board, 1999.

injuries or diseases such as diabetes or asthma where everyone is at risk. Of course, the numbers would look different if we considered individual age groups. Unintentional injuries are the leading cause of death for people from 1 to 34 years old, as might be expected for this relatively healthy age group. However, behavior and habits early in life can enhance or diminish our chances of death from a number of causes later in life. Nevertheless, such simple calculations allow people to appreciate the relative magnitude of the risk of death by various causes. People can use the numbers in Table 13.1 and make lifestyle changes that reduce their risk for those causes of death, or compare the risk from exposure to contaminants in the environment to risks that are an inherent part of life. The last use of the numbers is of most interest in this chapter. The ability to quantify risk is an important step in a logical approach to human and ecological risk.

The general public can make a number of responses to risks and these responses are not mutually exclusive. The risk can simply be avoided or eliminated. This strategy was utilized for chlorofluorocarbons (CFCs) used as propellants in aerosol cans and as a refrigerant, or with the pesticide DDT. In both cases the substances were banned and, fortunately, substitutes are available. Regulation or modification of the risk can be employed to reduce the frequency or magnitude of the negative outcome. For example, flood-control structures can be used to reduce the frequency that floods will affect an area or limitations on the amount of a substance (e.g., N, P, pesticides, or trace elements) that can be applied to soils can be used to reduce the negative outcomes associated with the exposure of organisms to those substances. The vulnerability of the exposed population can be reduced. In this case, the risk event is not changed but the people potentially affected by it may receive advance warning and be able to reduce their losses. Several post-event strategies are often used. Better ambulance service can be implemented in response to traffic accidents, thus increasing the chance for surviving an accident; however, the chance of being in an accident does not change. Insurance also provides financial reimbursement for monetary losses.

Risk assessment is a process by which we attempt to determine the probability and magnitude of injury, loss, or damage that may result from a potential health hazard to organisms. *Risk management* is a process by which economic, political, legal, and ethical ramifications of the results of risk assessment are considered. Regulatory decision making is based on both risk assessment and risk management. Environmental issues can be very emotional because they potentially involve human health and economic impacts. Overall, risk assessment provides a scientific basis for the creation of environmental regulations or the determination of cleanup levels, although there is no guarantee that risk assessment results will actually be used when the final decisions are made. Regulations or cleanup efforts may be overprotective or underprotective because of politics or economics.

There are a number of philosophical issues that need to be presented in relation to quantifying risk and the risk assessment process. The first is the concept of *negligible risk* vs. *absolute or zero risk*. Negligible risk implies that there is some very small but nonzero chance that the negative outcome will occur, whereas absolute or zero risk implies that there is no chance the negative outcome will occur. The phrase “acceptable level of risk” is often used for something that has negligible risk. The regulation of cancer-causing substances is an excellent example. Exposure to some potentially carcinogenic substances is regulated such that the increased risk of cancer due to the exposure is on the order of 10^{-5} to 10^{-6} , meaning that 1 out of 100,000 or 1 out of 1,000,000 people exposed might develop cancer. Compared with the risk values in Table 13.1, these risk levels are quite small and would be difficult to detect statistically compared with background cancer rates (about 0.03 over a lifetime). This level of risk is often called *de minimis risk*, or a risk too small to be of concern to society. Alternatively, some might say that in a city of 1 million there would be an increase of 1 to 10 preventable cancer cases. Now if the exposure to the potentially carcinogenic substance resulted in some benefits for society, or would cost a great deal of money to prevent, some might consider 10^{-5} to 10^{-6} an acceptable level of risk and the resulting regulations would be considered a negligible risk standard. If regulations were such that no exposure was the only acceptable scenario, the regulations would be considered

an *absolute or zero risk standard*. There is no risk if there is no exposure. Generally, regulations use the negligible risk approach.

A cost–benefit approach is often used for environmental issues. A chemical company cannot obtain a label for a new pesticide unless it proves that the pesticide has some benefits compared with pesticides currently on the market and that the environmental costs and risks are acceptable (see Chapter 10, Environmental Quality Issues/Events: Process Involved in the Registration of a New Pesticide). Alternatively, we can consider the cost of cleaning up a contaminated site vs. the benefits of preventing human health problems or ecological damage. Eventually, a point is reached where additional money spent on cleanup yields little additional benefits, even though the site may not be as clean as some would like it to be.

A new challenge in risk assessment will be the study of risk from the use of genetically modified organisms (GMOs) that were discussed in Chapter 10. Two examples of GMOs that are already in use are glyphosphate-resistant crops (e.g., corn, soybean, cotton, rice) and Bt-corn that has had a gene added from a soil bacterium (*Bacillus thuringiensis* subsp.) that produces a protein that is toxic to the European corn borer. Glyphosphate is a nonspecific herbicide and, when used in combination with a resistant crop, can provide effective weed control and other significant advantages in crop production. Here the potential effects from the use of the GMOs are much less clear and include the possible transfer of genes to other or related species (gene flow) or subtle ecological effects on plant populations. The extent to which these effects will occur is not known, nor is it known whether these effects are necessarily negative. One clear advantage to using glyphosphate-resistant crops is that there is reduced use of other herbicides (e.g., atrazine) that have known human health effects.

We must also be cautioned against becoming too comfortable with the risk numbers and concluding that any risk at the 10^{-5} to 10^{-6} level or less is acceptable because of the comparison with higher risks associated with other activities. In general, we must strive to keep risk levels low and avoid unnecessary exposure to potentially harmful substances as a safety margin. For example, scientists are just beginning to appreciate the toxicological effects of exposure to chemical mixtures. In some cases exposure to two substances at low levels can have a greater effect than exposure to either substance individually. Pharmaceuticals, personal care products, and endocrine disruptors are relatively new concerns that warrant careful consideration of environmental risk.

A philosophical approach that has become somewhat formalized in the risk assessment area is that of the *precautionary principle*. Definitions vary, but the basic concept is that, in the absence of scientific evidence that something is safe, a conservative approach should be adopted. The burden of proof for safety lies with the proponent of the new substance or technology and not with the general public. Opponents argue that nothing can be proved entirely safe and the adoption of the precautionary principle would cause undue hardship and may, in some cases, actually cause harm. Several current issues, notable GMOs and global climate change, are interesting studies in the precautionary principle. Some countries have clearly taken a conservative approach while others have not. At this point, there is no way to tell which approach is more appropriate. Overall, we can find examples where the precautionary principle was successful in averting larger problems and others where it was a hindrance toward progress.

13.2 RISK PERCEPTION

A discussion of risk assessment would not be complete without consideration of the general public's perception of risk as compared with that of the scientific community. As we might suspect, the perception of risk by these two groups can be quite different and their response may also be contradictory. For example, surveys have revealed that people generally feel that they face more risks today than people faced in the past. This is despite the fact that average life expectancy has increased in recent times. Risk perception is a key element in how a government regulates environmental issues and in the opposition of new technologies that may pose a threat to the environment.

Table 13.2 Over- and Underestimated Frequency of Death as Judged by Laypeople

Overestimated	Underestimated
Tornadoes	Asthma
Floods	Stomach cancer
Pregnancy	Diabetes
Botulism	Stroke

Source: Slovik, P. et al., *Environment*, 21, 14, 1979.

Early work in risk perception established that laypeople overestimate the frequency of rare causes of death while underestimating the frequency of more common causes of death, as illustrated in Table 13.2. Far fewer people die as a result of tornadoes, floods, pregnancy, and botulism than are estimated to die by laypeople. The actual number of deaths per year in the United States from any of these causes is less than 1000. Likewise, far more people die from asthma, stomach cancer, diabetes, and strokes than were estimated. More than 100,000 people die from strokes per year, for example. This information indicates that familiarity with the cause of death induces a bias in perception of the risk. A death as a result of botulism is quite unusual and would likely be reported by the news media. Since people are not familiar with botulism as a cause of death, the noteworthy status of the death would raise their consciousness of the cause and could make them perceive that botulism is more prevalent than the number of cases reported. A death as a result of a stroke would not be a newsworthy item and, over time, the awareness of the magnitude of this cause of death would diminish.

The psychometric model is often employed to identify factors that influence risk perception by the general public. Earlier work in this area established that as the number of people exposed to the risk, dread, and the newness of the activity or issue increased the perceived risk increased. Slovik (1987) published a classic paper on this in which the factors were combined into a two-dimensional psychometric diagram that is summarized in Table 13.3. Here the two primary factors involved in risk perception by the general public are dread and knowledge (whether the risk is known or unknown). Dread is an intense fear that something bad might happen. Within each major factor are subfactors that can enhance or reduce our perception of risk. An accident or activity that invokes dread and is relatively unknown will be perceived as the most risky, whereas an accident or activity that does not invoke dread, and is familiar, will be perceived as the least risky. This has led to the observation that many people have the greatest fear of the least likely events and the least fear of the most likely events. Obviously, many accidents or activities fall somewhere in the

Table 13.3 Factors Associated with Risk Perception by the General Public

Risk Perception Factor	Subfactors for High or Low Risk Perception	
	High	Low
Dread	Uncontrollable	Controllable
	Globally catastrophic	Not globally catastrophic
	Fatal consequences	Consequences not fatal
	Not equitable	Equitable
	Involuntary	Voluntary
Knowledge	Effects not observable	Observable effects
	Unknown to those exposed	Known to those exposed
	Effects delayed	Effects immediate
	New risk	Old risk

Source: Slovik, P., *Science*, 236, 280, 1987.

middle in that they may invoke dread but are familiar to us, or vice versa. Whether the risk is undertaken voluntarily or not is also an important consideration. A person smoking a cigarette is at much greater risk from tobacco smoke than nonsmokers subjected to passive smoke, yet the nonsmokers will have a greater objection to the risk than does the smoker.

More recent work with the psychometric model has identified activities that “tamper with nature” as an additional factor in risk perception. Thus, GMOs and some aspects of nuclear energy, both of which seem unnatural, would have a high perception of risk. The opposite is also true. Herbal remedies have greatly increased in popularity in recent years in part because they are viewed as a “natural” treatment for various symptoms. However, an herbal remedy that is proven effective (using the scientific method) most likely has an active ingredient responsible for this effect. There is no scientific reason to believe that an active ingredient produced by a plant is potentially less harmful than one produced by synthetic means. Many highly potent toxins are produced in nature.

Covello and Sandman (2001) describe perceived risk as the sum of hazard and outrage (risk = hazard + outrage). Hazard refers to the quantifiable risk as described in the previous section. Outrage is the modifier that accounts for the qualitative influence of a number of factors on risk perception. The outrage factors are voluntariness, controllability, familiarity, fairness, benefits, catastrophic potential, understanding, uncertainty, delayed effects, effects on children, effects on future generations, victim identity, dread, trust, media attention, accident history, reversibility, personal stake, ethical/moral issues, and human vs. natural origin. For each factor it is not difficult to see how it could enhance the perception of risk. A few examples are given below.

Control is a major subfactor in risk perception. When we feel we have control of an activity our perception of the risk is much lower. Driving an automobile is a good example. If you needed to travel 2000 km you could roughly estimate from Table 13.1 that you would be approximately 300 times safer flying to your destination than driving. More accurate calculations using passenger miles indicate that flying is approximately 50 times safer than driving. Many people would feel safer driving, however, because they are in control of the automobile (and probably think they are good drivers). When you fly, nearly all aspects of the trip are out of your control. In addition, the thought of an airplane crash invokes dread as often there are no survivors. In the period from 1993 to 2002, an average of approximately 137 people per year were killed in commercial aviation accidents in the United States while more than 40,000 were killed each year in automobile accidents. Despite these figures, many people are still not convinced that they should wear their seatbelts while driving. The classification scheme shown in Table 13.3 identifies many of the important considerations for how risk is perceived by laypeople and allows us to predict qualitatively how the public will perceive a risk. The previously cited example of driving illustrates the concept of risk denial. *Risk denial* is the difference between the actual risk from an activity and the perceived risk by an individual. In this case, people perceive the risk as being much less than it actually is, as is often the case, and risk denial is high.

An additional factor that helps explain variations in risk perception by the public over time is that reports of accidents or events serve as signals. This simply means that the public's awareness of a risk, however small that risk may be, is greatly increased by a major event or accident. The Three Mile Island and Chernobyl nuclear accidents made the public's perception of risks from nuclear energy increase dramatically and have played a major role in slowing or stopping the use of nuclear energy in the United States. In the future, we may have to rely more on nuclear energy as a means of addressing global climate change from greenhouse gases. More recently, the terrorist acts of September 11, 2001 raised our consciousness of the possibility of such acts against a nuclear facility and removed the gains in public support for nuclear energy that had developed since Three Mile Island and Chernobyl. The crash of a commercial airliner in general certainly will receive media coverage and will at least cause a temporary reduction in the number of people willing to fly; yet the total number of people killed in automobile accidents goes relatively unnoticed in society.

Table 13.4 Significant Differences in Perceived Risk from Global Climate Change between Laypeople and Experts

Issue	Range (1–7)	Mean Ranking	
		Layperson	Expert
Species loss	None → Great	4.6	3.6
Animal/plant suffering	None → Great	4.8	4.0
Human health threat	None → Great	4.3	3.6
Infringement on rights of nonhumans	Does → Not Greatly	4.6	3.9
Human suffering	None → Great	4.4	3.8
Societal benefits	None → Many	2.6	3.1
Scope of impacts	Small → Widespread	4.6	4.1
Media attention	None → Great	3.8	3.3
Overall risk	None → Great	4.5	4.1
Negative emotion	None → Great	4.8	3.7
Adaptability of environment	Not at all → Very	3.7	4.1
Acceptability for environment	Not at all → Completely	3.5	3.9

Note: Each group was asked to rank the risk issue on a scale from 1 to 7.

Source: Lazzo, J. K. et al., *Risk Anal.*, 2, 179, 2000.

Technological advances present a dichotomy of sorts for risk perception. Such advances can increase the perceived risk because they are not understood by the general public while at the same time the public often relies on technological advances as a salvation from risk. Predictably, the public has a perception of high risk from GMOs that will likely decrease with time provided that new information suggesting actual risk does not surface. The perceived risk from new environmental concerns by the general public is handled in a similar fashion. Table 13.4 illustrates the heightened concern of laypeople as compared to experts with regard to global climate change.

The public's perception of risk places regulatory agencies in somewhat of a quandary. While they are public agencies designed to respond to public needs and concerns, they cannot justify the allocation of scarce resources to problems that are perceived to be much worse than reality.

13.3 CARCINOGENICITY

The risk assessment procedures that are followed are influenced by whether or not the substance has been shown to be carcinogenic. The EPA has a classification scheme for carcinogenicity based on human and animal evidence. This scheme is outlined in Table 13.5. Substances in Group A are known human carcinogens (e.g., radon, vinyl chloride), Group B refers to probable human carcinogens, Group C refers to a possible human carcinogen, Group D refers to something that is unclassified because of inadequate data, and Group E refers to a substance with evidence of noncarcinogenicity. For regulatory purposes Groups A and B are collectively called Category I, Group C is called Category II, and Groups D and E are referred to as Category III.

As an example of how the classification may influence the regulatory process, we can use the maximum contaminant level goals (MCLGs) for drinking water. The MCLG is the desired maximum concentration for a substance in drinking water, which considers all its potential harmful effects. The MCLG for any Category I substance is zero while those for Category II and Category III substances are nonzero values calculated in various ways. A concentration of zero is not obtainable and the actual drinking water standard is called the maximum contaminant level (MCL). The

Table 13.5 Carcinogenic Categorization of Substances Based on Animal and Human Data

Human Evidence	Animal Evidence				
	Sufficient	Limited	Inadequate	No Data	No Evidence
Sufficient	A	A	A	A	A
Limited	B1	B1	B1	B1	B1
Inadequate	B2	C	D	D	D
No data	B2	C	D	D	E
No evidence	B2	C	D	D	E

Note: Group A substances are known human carcinogens; Group B1 substances are probable human carcinogens based on limited evidence of carcinogenicity from human epidemiological studies; Group B2 substances are probable human carcinogens based on sufficient evidence of carcinogenicity from animal studies; Group C substances are possible human carcinogens; Group D substances are not classified due to inadequate data; and Group E substances have evidence of noncarcinogenicity.

regulations require that the MCL be as close to the MCLG as possible with the best available technology for removing that substance from the water. Obviously, this process tends to force the MCL to be lower for Category I substances than for Category II or III substances.

Cancer death rates in the United States have received some attention in recent years because the overall rate has been increasing for some time. The overall rate is the average across all types of cancer. Some believe that increasing cancer death rates are a result of exposure to anthropogenic chemicals in our environment and are a signal that more restrictive environmental regulations are needed. While we cannot say for certain that our environment is responsible for the increasing cancer rates, evidence suggests there are other factors that at least partly explain the changes. One is that the average age of the population is increasing. Cancer death rates increase with age, so the overall increase in cancer rates is partially a reflection of an older population. There are also some types of cancer associated with smoking that have increased because of increasing numbers of people who have smoked for long periods of time and because the number of women who smoke has dramatically increased. And, of course, cancer treatments have made tremendous advances in the last 20 years. Still, the death rates for some types of cancer have increased without explanation, and therefore environmental factors cannot be ruled out.

13.4 RISK ASSESSMENT

The risk assessment process has evolved considerably over the past 20 years. Early formalization of the process identified four steps: (1) hazard identification, (2) exposure assessment, (3) dose–response assessment, and (4) risk characterization. This process, which is still in use today, is generally applied to individual stressors and potential adverse effects on a single organism or small group of organisms. The most typical application is for human health risk assessments with some use for ecological risk assessment. The emphasis is on direct toxic effects of a stressor on the organism. Today, the formal ecological risk assessment process takes a broader view of the ecosystem and includes steps beyond the four listed above. These additional steps are discussed in a following section.

Risk assessments are complicated endeavors that span many areas of expertise and invariably involve the use of assumptions and seemingly arbitrary safety factors that are sources of criticism. Several recent examples on a national scale include risk assessments for emissions from incinerators, dioxins, lead, use of cement kiln dust as an agricultural liming agent, and land application of municipal biosolids. The last was mentioned previously and is discussed in more detail in Section 13.4.1. Risk assessments are also often performed for various contaminated sites and are more local in scope. The risk assessment for emissions from incinerators, for example, had to consider

inorganic and organic contaminants and was required to take into account dispersion of contaminants into the atmosphere; potential human health and ecological risks from direct inhalation of contaminants; wet and dry deposition of contaminants onto soil, water, and plants; uptake of contaminants by plants from soil or by direct deposition; potential human health and ecological risks from contaminants in plants; the influence of contaminants on aquatic organisms; and potential human health and ecological risks from contaminants in the aquatic organisms.

For our purposes, the overall goal of a risk assessment is to consider existing or possible contamination of soil, air, water, or sediments; trace all possible routes of exposure for organisms of concern; determine the dose received by organisms of concern; and determine the potential negative impacts of that dose on the organisms of concern.

Hazard identification is a qualitative assessment of a substance that determines whether exposure to a specific substance causes harm. One way for a substance to be found harmful would be through simple epidemiological studies in which the frequency of disease was found to be higher in an exposed group compared with an unexposed group. Under the Toxic Substances Control Act (TSCA), any new substance is considered to be a hazard until proved otherwise. The combination of exposure assessment, dose–response assessment, and risk characterization is sometimes referred to as quantitative risk assessment.

The U.S. EPA maintains a database called the Integrated Risk Information System (IRIS), which provides information on the toxicity of many substances (see <http://www.epa.gov/iris>).

13.4.1 Exposure Assessment

Exposure assessment is the process by which the identity of the organisms exposed to a contaminant and the dose received are determined. All possible means of exposure to a contaminant and the relative contribution of each route of exposure to the dose of the recipient are investigated. We need to consider how the organism can receive a dose as a starting point. Humans and animals, for example, can be exposed via inhalation, dermal exposure, or by ingestion (see Figure 1.2). Therefore, air quality, chance of dermal contact, and the possibility of the pollutant entering the digestive tract must be considered in exposure assessment. Plants have analogous pathways for exposure. Plants obtain nutrients, contaminants, and water from soils, and are sensitive to changes in soil composition. Plants respire and photosynthesize and therefore respond to changes in air quality. Substances can also be absorbed on the waxy surfaces of leaves, similar to dermal exposure in humans, and dust fall and quality of soil and water contacting the leaves must be considered.

An excellent example of exposure assessment relative to potential soil contamination is that done for the EPA biosolids disposal regulations approved in 1993. Of interest to this discussion are the limits for the total amount of trace elements that can be applied to soils via land application of municipal biosolids (see Table 9.2). Table 13.6 lists the exposure pathways considered in the risk assessment process for these regulations. While these pathways were used specifically to consider land application of municipal biosolids, in a general sense they could be appropriate for anything contained in or applied to soils (e.g., pesticides, animal manures, fertilizers). The number or types of pathways would vary, of course, depending on the fate and transport mechanisms of the pollutant. Each pathway has an organism as an end point and the potential negative effects on the organism are the concern.

One of the steps in exposure assessment for the biosolids regulations was to identify the most sensitive pathway for each trace element. The most sensitive pathway refers to the pathway by which an adverse effect could occur at the lowest soil contaminant concentration. Examples include pathway 8 for boron (B), zinc (Zn), copper (Cu), and nickel (Ni) where phytotoxicities limit plant growth before negative effects on other organisms are thought to occur; pathway 3 for Pb and fluorine (F) where direct consumption of soil causes the greatest problems; pathway 6 for molybdenum (Mo) and selenium (Se) where ruminant animals suffer molybdenosis or selenosis, respectively, because of plant uptake of these elements that occurs without the plants themselves

Table 13.6 Pathway Models for Land Application of Municipal Biosolids

Pathway	Description of Highly Exposed Individual (HEI)
1: Biosolids → soil → plant → human	Individuals with 2.5% of all food produced on amended soils
2: Biosolids → soil → plant → human	Home gardeners with 1000 Mg/ha, 60% garden foods for lifetime
3: Biosolids → soil → human child	Ingested biosolids product, 200 mg/day
4: Biosolids → soil → plant → animal → human	Farms, 45% of home-produced meat
5: Biosolids → soil → animal → human	Farms, 45% of home-produced meat
6: Biosolids → soil → plant → animal	Livestock feeds, 100% on amended land
7: Biosolids → soil → animal	Grazing livestock, 1.5% biosolids in diet
8: Biosolids → soil → plant	Phytotoxicity, strong acidic amended soil but with limestone added to prevent natural aluminum and manganese toxicity
9: Biosolids → soil → soil biota	Earthworms, microbes, in amended soil
10: Biosolids → soil → soil biota → predator	Shrews (<i>Sorex araneus</i> L.), 33% earthworms in diet, living on site
11: Biosolids → soil → airborne dust → human	Tractor operator
12: Biosolids → soil → surface water → human	Subsistence fishers
13: Biosolids → soil → air → human	Farm households
14: Biosolids → soil → groundwater → human	Well water on farms, 100% of supply

Source: Chaney, R. L. et al., Soil root interface: ecosystem health and human-food-chain protection, in P. H. Huang et al., Eds., *Soil Chemistry and Ecosystem Health*, SSSA Spec. Pub. No. 52, Soil Science Society of America, Madison, WI, 1998.

experiencing phytotoxicities or before other organisms are at risk; and pathway 1 for cadmium (Cd) where food chain transfer to humans is the greatest concern. The fate and transport mechanisms for these trace elements in soils clearly play a role in determining which pathway ends up being the most sensitive. For example, Pb is strongly sorbed by soils to the extent that plant uptake and, consequently, food chain transfer to humans or animals is of little importance, whereas direct consumption of soil is of great concern. Cadmium, on the other hand, is readily taken up by plants and is easily moved from the soil into the food chain.

In conjunction with the determination of the most sensitive pathway is the definition of highly exposed individuals (HEIs), those persons with exposure greater than that of 95% of the population and with the greatest likelihood of suffering the greatest harm at the lowest dose of the pollutant. Alternatively, the high end exposure estimate (HEEE) is the person receiving the dose greater than the 90th percentile of all individuals in the population. The HEI and HEEE represent a subdivision of a group of organisms. The basis for the division might be gender, age, use of tobacco, dietary habits, sources of food, or geographical location. The HEIs for each pathway used for the biosolids disposal regulations are also given in Table 13.6. Other examples of HEIs include infants, for nitrates in drinking water, or predatory birds or people whose diet is composed mainly of fish, for DDT. The premise behind the HEI concept is that if regulations protect the most exposed and sensitive individuals in the most sensitive pathway, then all other individuals will be protected as well. In practice, an HEI is not used for all risk assessment calculations. Where the HEI is used, however, the selection of an appropriate HEI is important. It is easy to construct a scenario that is so restrictive that there are no individuals within the population who fit the full description of the HEI. When this occurs, the calculations are for a risk that cannot exist and the results are overly protective.

To determine dietary exposure for humans, an accurate determination of what is consumed by people must be made. This is accomplished with a total diet study. The total diet study incorporates a survey of consumers that determines how much of various food groups are consumed by various gender and age categories of the population. If the composition of one or more of the food groups changes, then the effect of that change on the population can be estimated. Data are also available on average water consumption by adults and children. A value of 2 L/day is often assumed for adults, although this is likely an overestimate for most individuals. Overestimating factors such as water or food consumption is another way to build safety into the risk assessment process. Soil ingestion by children has also been extensively studied. Most children between the ages of 1 and 6 will consume less than 0.03 g of soil/day with the contribution from indoor dust vs. outside soil ranging from 0 to 100%. Some children with pica (habitual ingestion of nonfood items), on the other hand, have been shown to ingest in excess of 8 g of soil/day averaged over 10 days of measurement.

13.4.2 Dose–Response Assessment

In a general sense, dose–response assessment establishes the relationship between the amount of a substance that an organism receives (the dose) and the effects on that organism (the response). Responses can be favorable or unfavorable. For the risk assessment process, dose–response assessment may take information from the exposure assessment and determine the effects on the exposed organisms.

Toxicologists often state that “the dose makes the poison” and point out that almost any substance can induce a toxic response at a high dose, and that most toxic substances can be tolerated by an organism at a low dose. In dose–response assessment we are generally interested in the effects of small doses of a contaminant on a population of organisms. The relevant questions are “at what dose will a measurable response occur” or, in the case of accidental exposure, “will a measurable response be found after a given dose was received.”

The type of response that is measured can vary considerably. Often, the type of response seems quite obvious for a risk assessment, such as an elevated cancer incidence as the dose increases or increased mortality rates for insects exposed to increasing doses of a contaminant. The responses may not always be so obvious, however, as sometimes the response is indirect. Changes in blood chemistry or tissue composition may be the indicator used for a particular contaminant for animals or humans rather than an actual disease or set of clinical symptoms. In ecological risk assessments the response may be changes in species diversity, density, or productivity.

Dose–response curves are often characterized as linear, with responses increasing proportionally to dose, or threshold, with no response until a critical dose is exceeded. A value that is sometimes calculated from dose–response experiments is the no observable adverse effect level (NOAEL). The NOAEL is the highest dose that can be administered without a statistically significant increase in adverse response. A linear dose–response curve, for example, predicts an increase in response with each incremental increase in dose, no matter how small the increment. The increase in response when the dose is greater than zero, however, must become large enough to be statistically significant. The NOAEL is a measure of how much the dose must be increased before a response occurs or before a threshold is surpassed. The NOAEL value is used in some risk assessment calculations.

As precise as the definition for the NOAEL is, few dose–response experiments actually use doses near the NOAEL value such that the NOAEL can be determined with a great deal of confidence. In fact, the doses used in animal experiments are typically much higher than humans are expected to receive. The primary reason for this is that the increase in response seen at the low doses expected in humans is so small that it would take an enormous number of laboratory animals exposed to the low doses over extended periods of time to obtain statistically significant results.

Thus, a major problem in dose–response assessment is the extrapolation of experimental results obtained from high doses to laboratory animals to the low doses that will actually be realized by humans. Several models may be used for this extrapolation. In general, a linear dose–response curve is assumed for carcinogenic substances and a threshold dose–response curve is assumed for noncarcinogenic substances, unless evidence exists to the contrary.

The extrapolation of results obtained from animal studies to humans is a second major problem in dose–response assessment. It is an accepted belief that substances known to cause cancer in humans will cause cancer in animals, but the opposite has never been conclusively shown. There are obvious ethical questions involved with dose–response experiments, primarily because we cannot perform studies with human subjects. In addition, epidemiological studies with human populations have limited value in identifying quantitative dose–response relationships. Thus, the use of laboratory animals for dose–response assessment, with all of the apparent shortcomings, is a necessary component of risk assessment.

13.4.3 Risk Characterization

Risk characterization combines the results from exposure assessment and dose–response assessment for determining the management practices or cleanup procedures that produce acceptable exposures to the receptor organisms. It is often a back-calculation, starting with an acceptable exposure to an organism and working back to the management practices or media concentrations (e.g., levels in soil or water) that produce the maximum acceptable exposures. Such calculations may form the basis for regulatory action.

A value that is often used in risk characterization is the reference dose (RfD). The RfD is the daily intake of a chemical that, if taken during an entire lifetime, will be without appreciable risk. The units of the RfD are typically mg/kg bodyweight/day. The RfD can be calculated as the NOAEL divided by a safety factor on the order of 10 to 1000, as is the case when animal data are being extrapolated to humans. The safety factor adjusts for comparisons between species and for studies using chronic, subchronic, or acute exposures. Several examples might best illustrate applications of the risk characterization process.

Example Problem 13.1

Atrazine is a herbicide commonly used to control weeds in corn and sorghum. One question that has been debated is whether atrazine should be classified as a Group B2 or Group C carcinogen. One study with one strain of rat found an increased incidence of mammary tumors after exposure to atrazine, but the EPA did not feel this was sufficient evidence to place atrazine in Group B2. Several studies determined NOAEL values for atrazine ranging from 0.48 to 5.0 mg/kg/day. The responses monitored in these studies included discrete myocardial degeneration in dogs to second-generation lower pup weights in rats. The EPA will typically use the lowest NOAEL for the calculation of the RfD. In this case, the RfD was calculated as 0.0048 mg/kg/day (the NOAEL divided by a safety factor of 100). From the RfD, the drinking water equivalent level (DWEL) was calculated as follows:

$$\text{DWEL} = \frac{\text{RfD} \times \text{BW}}{I_w}$$

where BW is the bodyweight of an adult (70 kg is typically used) and I_w is the drinking water consumed by the person in a day (2 L/day). The DWEL value is the maximum allowed drinking water atrazine concentration assuming the person obtains all of his or her atrazine from the water. In this case the DWEL is 0.168 mg/L.

The next step is to calculate the MCLG, which is calculated one of two ways. The preferred way is to adjust the DWEL based on the amount of the chemical obtained from other sources, such as food and air. If this information is not available (the usual case), then the MCLG is calculated assuming that 20% of the chemical is obtained from drinking water. An additional safety factor of 10 is used for atrazine since it is a Group C carcinogen. This results in an MCLG of

$$\frac{0.168 \text{ mg/L} \times 0.2}{10} = 0.003 \text{ mg/L}$$

The best available technologies allow the MCL to be the same as the MCLG for atrazine and the drinking water standard became 0.003 mg/L (3 ppb). Any public drinking water supplier whose average atrazine concentration exceeds 3 ppb must take steps to reduce it. Atrazine can be removed from water with charcoal filtering, although the process is expensive.

Considerable debate has arisen over atrazine. Some parties feel that sufficient evidence exists to ban atrazine altogether. Atrazine users feel that it is an important tool (effective and inexpensive) in crop production and that atrazine is safe when used properly. The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) is the legislation that covers the labeling of atrazine. It stipulates that atrazine should perform its intended function without unreasonable adverse effects on the environment. Unreasonable adverse effects are described as any unreasonable risk to humans or the environment, taking into account the economic, social, and environmental costs and benefits of the use of atrazine. Clearly, the law provides a need to balance risks or costs against benefits. Currently, the weight of evidence is on the side of benefits for atrazine. The cost issue is important in this case because of the high cost of charcoal filtering. Public water supplies that use a high proportion of surface water as a source may have problems meeting the 3 ppb atrazine standard if atrazine is used extensively in the drainage area of the water source. In one unique case, a pesticide management area was established in Kansas around a reservoir that places more stringent rules on the use of atrazine than required by the product label. Compliance is voluntary at this point and atrazine levels have declined. If the concentrations had not declined, the rules may have become mandatory.

A second example of risk characterization pertains to the allowable cumulative application rate of a contaminant to soil via land application of municipal biosolids, as was described previously in Chapter 9 and Table 9.2. The reference application rate (RP, kg/ha) is calculated as in the following example.

Example Problem 13.2

$$RP = \frac{\left(\frac{RfD \times BW}{RE} - TBI \right) \times 10^3}{\sum UC_i \times DC_i \times FC_i}$$

where RP, RfD, and BW are as defined before, TBI is the total background intake rate of the contaminant (mg/day), RE is the relative effectiveness of ingestion exposure (unitless, generally assumed to be 1 unless evidence exists to the contrary), 10^3 is a conversion factor (mg/mg), UC_i is the uptake response slope for the food group i (mg/g dry weight per kg of contaminant applied per ha), DC_i is the daily dietary consumption of the food group i (g dry weight/day), and FC_i is the fraction of food group i assumed to originate from biosolids-amended soil (unitless, assumed to be 2.5% for the population as a whole). The value of DC_i is determined from the total diet study. Calculate RP when RfD = 0.001 mg/kg day, BW = 70 kg, RE = 1.0, TBI = 0.0161 mg/day, and $UC_i \times DC_i \times FC_i = 2.5 \text{ mg ha/kg day}$. (Data from Chaney et al., 1998.)

$$RP = \frac{\left[\frac{0.001 \times 70}{1.0} - 0.0161 \right] \times 10^3}{2.5} = 21.6 \text{ kg/ha}$$

Although the actual calculations are cumbersome, the reader should appreciate several aspects of the equation given at the beginning of this example problem. The equation is written with a human as the receptor organism, although it could be used for any organism, provided the appropriate data are available. The numerator determines the allowable effective dose of the contaminant to the receptor organism above the background level. The denominator determines the increase in the contaminant concentration in each food group as the contaminant is added to the soil and factors in how much of that food group is consumed and the proportion of that food group that originates from soils affected by the contaminant. In the case of direct soil ingestion, the denominator is modified to reflect the change in soil contaminant concentration as the contaminant is added to the soil and the soil ingestion rate. Additional safety factors may also be added.

Recall from Chapter 9 that trace element contamination of soils is essentially permanent. Therefore, it must be recognized that the municipal biosolids disposal regulations allow a certain amount of irreversible soil contamination to occur. This is in contrast to the Western European philosophy that argues that soils have a finite capacity to absorb pollutants without negative consequences and that humans should not use up any of that capacity (i.e., soil concentrations should not be allowed to change). The U.S. regulations were written with a risk vs. benefit philosophy. The risk assessment process indicates the increase in risk can be regulated to insignificant levels and there are considerable benefits for land-applying biosolids. Land application of biosolids can save money compared with other disposal options. For example, placing the material in a landfill has become prohibitively expensive in recent years and has associated risks such as leachate generation and the potential for contamination of groundwaters and surface waters. Incineration or ocean dumping are no longer considered environmentally acceptable. The biosolids also contain plant nutrients and organic matter that can benefit soil physical properties and soil fertility. Finally, national regulations might actually reduce risk in areas where biosolids disposal was not previously regulated. More recent research in Europe suggested that metals in biosolids can influence soil microbial activity at soil concentrations below that allowed by U.S. regulations, although such effects may occur under only very unique situations. Such impacts on the soil environment were not considered in the risk assessment for biosolids because such data were not available at the time. In addition, risks associated with pharmaceuticals that pass through wastewater treatment facilities and end up in biosolids have yet to be determined. Whether the risk assessment should be expanded to include these effects is a value judgment that must be made by society.

Results from human health risk assessments for noncarcinogenic substances are often expressed in terms of a hazard index or hazard quotient. The hazard index is simply the dose received divided by the reference dose for that substance. If the hazard index exceeds 1, then the risk is unacceptable because the reference dose has been exceeded. For substances that are regulated as carcinogens, a slope factor is used. The slope factor is determined from a dose–response curve and represents the increase in the incidence of cancer per unit increase in dose. When the dose is determined by the previous steps, we can estimate the resulting cancer incidence rate or risk and decide whether that level is acceptable or not. Typically, cancer risks above 10^{-6} to 10^{-4} are considered too high. Figure 13.1 shows a hypothetical dose–response curve for a possible carcinogenic substance in drinking water. Linear and threshold response curves are shown for comparison as are the actual range of doses used in animal studies and the anticipated range of human exposure. Often the linear response is assumed, as it is a more conservative estimate of risk, despite toxicological evidence that a threshold response may be more realistic. This figure also illustrates the two problems with dose–response assessment that were discussed earlier.

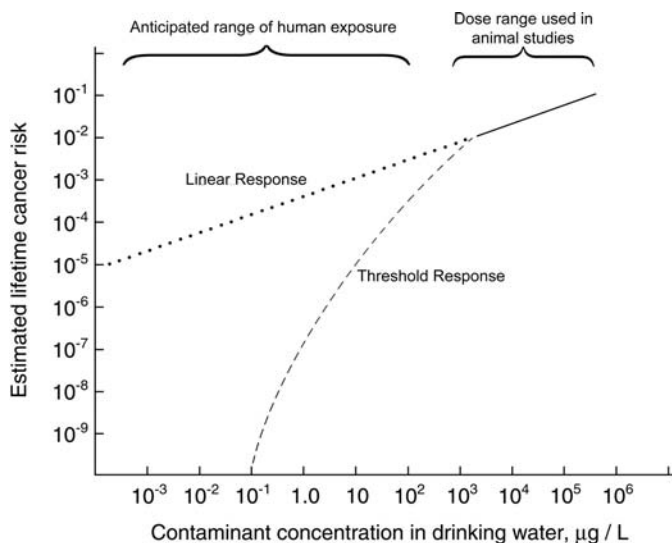


Figure 13.1 Hypothetical dose-response curve for a carcinogenic substance showing the actual doses used in animal studies and the anticipated doses that humans will receive. The assumed dose-response relationships at low doses illustrate the potential impact of the assumption on risk estimates.

Once an algorithm is developed for evaluating risk for a given exposure pathway, parameters can be easily manipulated to evaluate the impact on the assessment of risk. The algorithm includes all of the assumptions that were utilized in the risk assessment. Assumptions are an integral part of risk assessment and are used to simplify the process, to account for missing or inadequate information, and to incorporate safety factors into the process. For example, if we are concerned about the impact of contaminant uptake by plants on the consumers of those plants, a value will have to be used for plant contaminant concentration. Assuming data are available, we could select an arithmetic mean, a geometric mean, or the 90th, 95th, or 99th percentile values. Each choice will affect the conservatism of the risk estimate, with a 99th percentile value more conservative than a 90th percentile value. Risks calculated with a stated set of assumptions and a defined algorithm are called deterministic risk estimations. Probabilistic risk estimations are sometimes used to augment deterministic estimations. A probabilistic risk estimation often uses a Monte Carlo simulation where the algorithm is run with ranges of values (based on a statistical distribution) for input variables. Each input variable is systematically varied across a reasonable range along with all other combinations of ranges for the remaining variables such that risk calculations are made for all possible combinations. This could alert the risk assessor to input variable combinations that produce unrealistic risk estimates. If no such unrealistic estimates are produced, it lends credibility to the deterministic approach that was used. This also helps improve confidence in risk estimations made with limited data.

13.5 ECOLOGICAL RISK ASSESSMENT

Ecological risk assessments may be performed to predict future adverse effects from an ecological stressor (prospective, e.g., the release of a new pesticide) or to determine whether a stressor has caused an effect (retrospective). Ecological risk assessments can also be used to characterize an ecological resource. The basic process followed in ecological risk assessment is similar to that described above (Figure 13.2). In general the problem formulation phase is similar to hazard identification, and the analysis phase, which includes characterization of exposure and

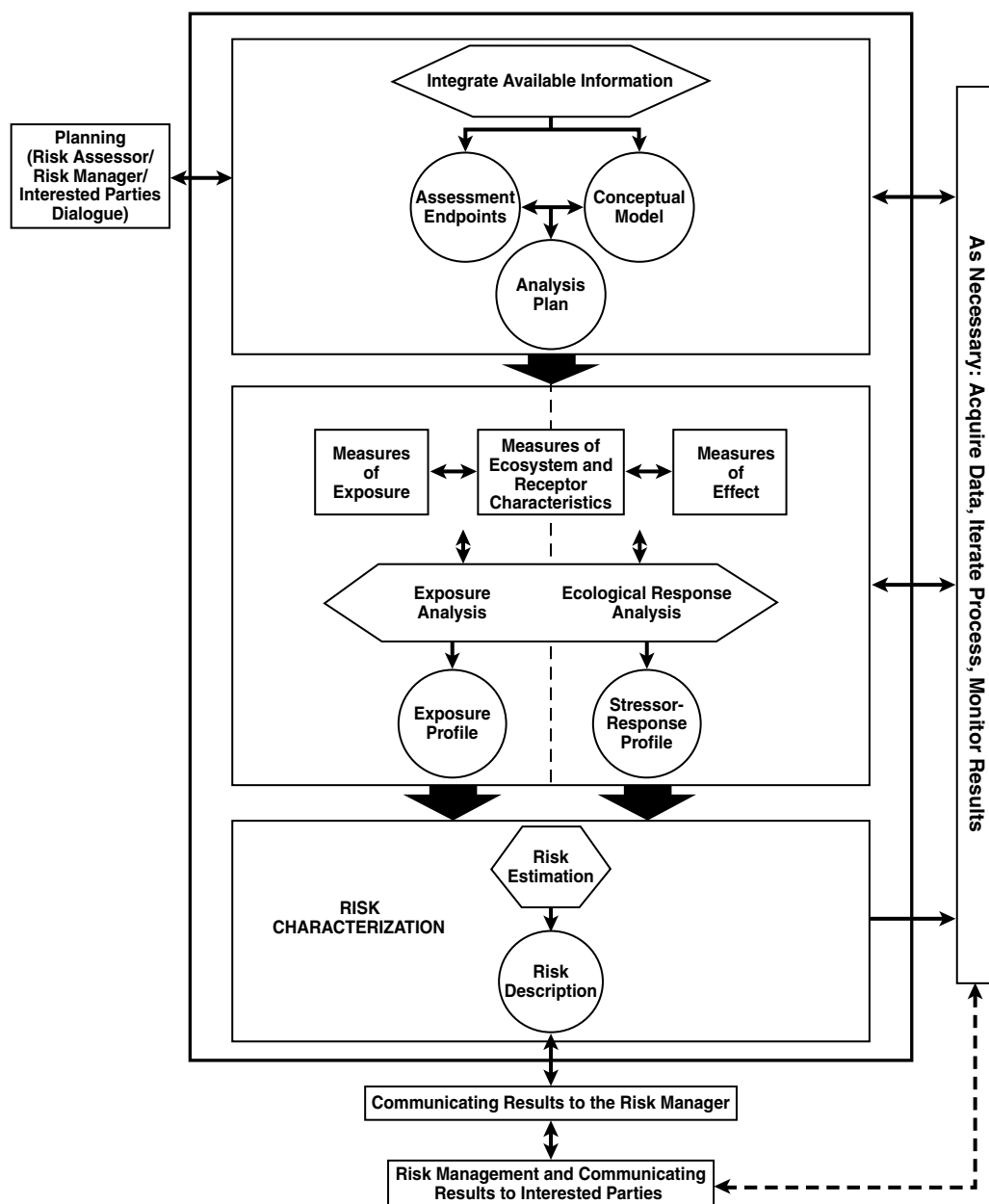


Figure 13.2 The ecological risk assessment framework, with an expanded view of each phase. Within each phase, rectangles represent inputs, hexagons indicate actions, and circles represent outputs. (From U.S. EPA, 1998.)

characterization of ecological response, is similar to exposure assessment and dose-response assessment. Both processes include a risk characterization phase.

The problem formulation phase differs significantly from hazard identification in that it includes selecting assessment end points and conceptual models. Assessment end points are used to overcome the difficulty in dealing with numerous species in an ecological risk assessment. Assessment end points are generally a species or species that are selected to represent the net effect of a stressor on different ecological organizational levels. Also, it is not practical to conduct a complete risk assessment for all potentially affected species. Even if it were practical, knowledge is lacking on

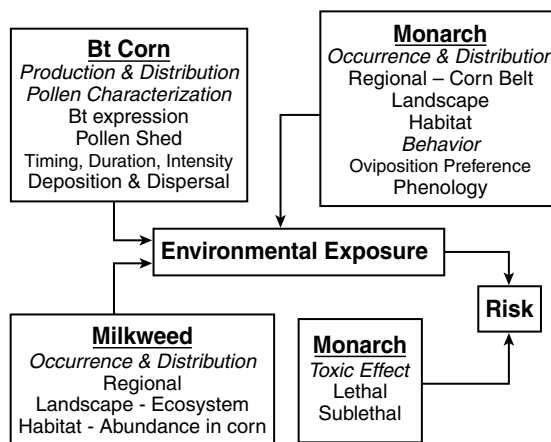


Figure 13.3 Conceptual model for ecological risk assessment for pollen shed by Bt corn and potential impacts on monarch butterflies. (From Sears, M. K. et al., *Proc. Natl. Acad. Sci. U.S.A.*, 98, 11937, 2001. © Canadian Food Inspection Agency. With permission.)

the behavior and feeding habits of many wildlife species. Assessment end points, or indicator species, may be selected to simplify the process. For example, exposure assessment for birds may be accomplished by using a representative species from those that primarily eat seeds (granivores), insects (insectivores), fish (piscivores), or earthworms (vermivores). Conceptual models present an overall approach to the risk assessment and often illustrate relevant questions and interactions that need to be considered. Figure 13.3 is a simple conceptual model for the potential effects of pollen generated from Bt corn on the monarch butterfly.

A considerable amount of effort is spent in the analysis phase conducting exposure assessment and dose–response assessment for the assessment end points, similar to the risk assessment procedure described previously. In risk assessments for contaminated sites, animals may be trapped and their exposure assessed by tissue analysis. Food chain modeling may also be employed. An example of a commonly modeled pathway would be seeds, mouse, and predatory birds where the concentration of the contaminant is followed up the food chain. For lipophilic substances such as DDT, polychlorinated biphenyls (PCBs), or methylmercury ($\text{Hg}(\text{CH}_3)_2$) tissue concentrations are bio-magnified between trophic levels with predators at the greatest risk. In addition to toxicological effects, habitat is also considered in the analysis phase. Habitat quantity or quality is not a factor that is normally expressed in a dose–response relationship, but can clearly influence the survival of a species.

Risk characterization is the final phase and generally involves some attempt to quantify the risk realized from the stressors. Attempts are made to draw conclusions about exposure and potential negative effects. Hazard indices may be employed here although widely accepted RfD values do not exist for wildlife species. A hazard index may be calculated using 10% of an acute dose, for example, in lieu of an RfD. A Tier 1 ecological risk assessment may stop at this point if hazard quotients do not indicate significant risk while a Tier 2, or more detailed, risk assessment may be undertaken if hazard quotients do indicate significant risk.

13.6 UNCERTAINTY

The risk assessment process is placed in perspective in Figure 13.4. Risk assessments are conducted in response to public pressures, existing environmental policies, or both. Once the process is complete, risk management takes over and eventually some regulatory action is implemented.

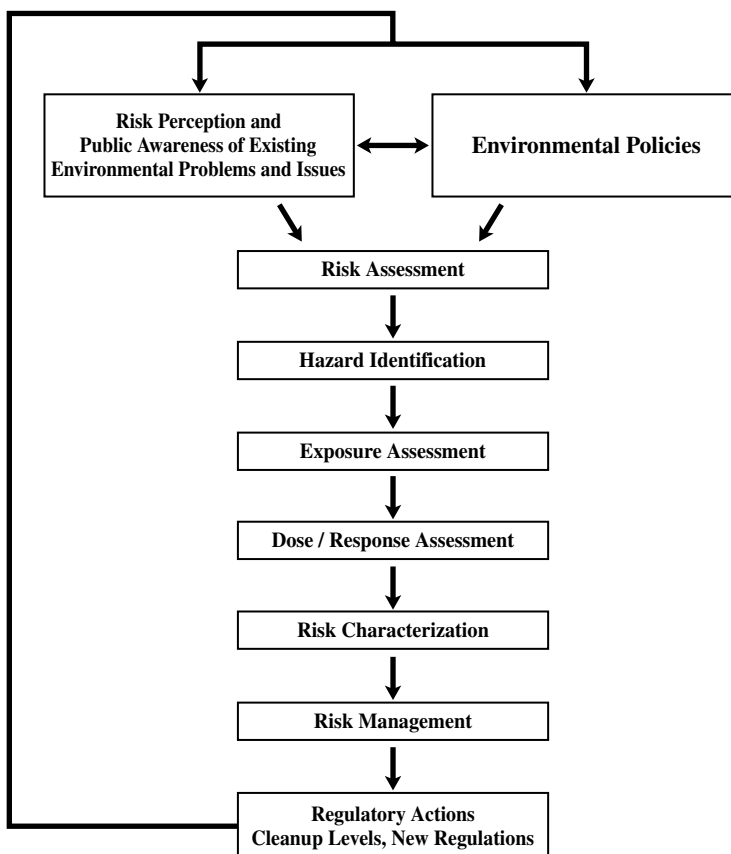


Figure 13.4 Flowchart for the risk assessment process.

This may be a cleanup level for a contaminated site or a new or revised environmental regulation. An important feature is the feedback loop. Once we have attempted to clean up a site or to enforce regulations, we may approach the risk assessment process differently in the future. Our perceptions of risk may change, we may become more accepting of present conditions, or we may have a better appreciation of the success or failure of regulations.

Both the general public and the scientific community can be critical of the risk assessment process and the resulting regulations. The general public often wants unrealistic levels of safety and, at times, seems to be unaware of the fact that a risk-free society cannot exist. The desired levels of risk are much lower than the risks realized from most everyday activities. Such reasoning led to the passage of the Delaney clause, which prohibited the use of cancer-causing agents as food or feed additives. The overall concept of the Delaney clause was sound except that it provides an absolute risk standard that does not take into account probability, costs, or benefits. The general public is also uncomfortable with arbitrary safety factors that it may not perceive as safe enough. In addition, increases in risk are often stated in terms of a few additional negative outcomes per 100,000 or 1,000,000 people exposed. This leaves the impression that preventable negative outcomes are deliberately allowed to occur.

The scientific community is critical of regulations that are written with limited or suspect data. Indeed, it is unusual to have the perfect data set, including dose-response information at the levels of actual exposure. The previously mentioned problems of extrapolation from high dose to low dose and from animals to humans have caused considerable debate. Both extrapolations require making predictions beyond the range of the data, which is generally not acceptable within the

scientific method. Scientists always want more data before they are comfortable in making a decision. Professional judgment is used often and, because of this, criticism of the risk assessment process is likely to continue indefinitely. It is helpful for both the general public and the scientific community to understand that the risk assessment process is not in quest of scientific truth. The goals are to estimate risk such that it is unlikely that the actual risk is underestimated and to develop regulations that will protect the environment without incurring unreasonable expense. Ultimately, environmental regulations and their implications for acceptable levels of risk are a social-political issue and not necessarily a scientific decision.

Environmental Quality Issues/Events

Lead Exposure and Human Health

Human health effects from Pb are an interesting study in risk assessment. Adequate data are available; the health effects from Pb are well established; there are numerous routes of exposure; exposure is easy to detect with a blood test; computer models exist that can be used to predict blood Pb concentrations; and, when soil Pb is involved, the bioavailability of that Pb can vary considerably and can possibly be reduced by soil management.

Hazard identification is not an issue with Pb as it is clear that exposure to Pb has negative consequences on human health. Young and unborn children are the most susceptible to Pb poisoning. Difficulties include premature birth, decreased birth weight, decreased mental abilities, learning difficulties, reduced growth in young children, and damage to the nervous system (hearing and balance problems), kidneys, and immune system. Acute Pb poisoning can affect adults and children alike; symptoms include abdominal cramping, elevated blood pressure, weakness in the extremities, anemia, and possible hearing loss. By far the problem of the greatest magnitude is chronic exposure to Pb in the environment by children.

Exposure assessment has identified numerous routes of exposure for children. In a home environment Pb can be ingested or inhaled from the diet, air, water, dust, soil, or leaded paint residues. If any of these media are enriched in Pb, the overall exposure can exceed critical values and the possibility of negative health consequences increases. Dietary exposure is generally not an issue unless the child consumes locally grown food that was produced in a high-Pb environment. Home gardening in a community affected by Pb smelting activities would be one example. There is little uptake of Pb by the plants themselves, but the consumption of unwashed or unpeeled vegetables (especially leafy vegetables and root vegetables such as potatoes, carrots, beets, or radishes) can lead to considerable Pb ingestion by the consumer. Inhalation of Pb from the air is also generally not an issue unless it is an urban area where leaded gasoline is still in use or where there are Pb-enriched particulates present in the air. Ingestion of Pb from water can be a significant source of Pb. Even without obviously contaminated drinking water sources, water in contact with old plumbing systems can have elevated background Pb exposure. Young children are in close contact with dust because they are frequently on the floor and exhibit hand-to-mouth activities. House dust mainly comprises carpet and fabric fibers, skin cells, animal dander, paint residues, and soil particles. If any of these components are enriched in Pb, the house dust will be as well. Adults, children, and pets constantly bring Pb-enriched particles into the home on their shoes or fur. Similarly, if the soil around a home has an elevated Pb concentration, there is a high likelihood that children will ingest some in their outdoor play activities. Leaded paint on the exterior or interior of the home will increase soil and dust Pb concentrations, but children can also directly ingest paint chips and increase their Pb intake.

The dose-response relationships for Pb intake are not clearly defined because of the many means of exposure and the numerous potential health effects. Blood Pb concentrations serve as a good indicator of Pb exposure and are often used to infer health effects. Some studies suggest, for example, that IQ test scores in children will decrease by 2 points for each 10 µg/dL increase in blood Pb concentrations. Overall, the current health guidelines suggest that blood Pb concentrations in children not exceed 10 µg/dL and that corrective actions be taken if the concentration exceeds 15 µg/dL. The average blood Pb concentration of children in the United States is less than the critical value. Estimates are that more than 50% of children in some inner-city areas exceed this guideline and surveys have shown greater than 20% exceedance in

some Pb-contaminated areas. Cessation of Pb in gasoline and solders has dramatically lowered blood Pb concentrations in the general public since about 1980.

Risk characterization is handled with the EPA Integrated Exposure Uptake Biokinetic (IEUBK) model, which takes into account all of the exposure routes for Pb in children, the internal adsorption/uptake mechanisms, and the various means of elimination of Pb from the body, and then calculates the resulting blood Pb concentrations. The components of the model are illustrated in Figure 13.5. We can use the IEUBK model with site-specific inputs to determine which exposure route results in the greatest impact on blood Pb concentrations in children. That information can then be used to determine which corrective actions would have the greatest benefit in reducing risk. Of particular interest in this book are the soil and dust input parameters. Both the Pb concentration and the bioavailability in these media can be specified in the model. As was shown in Table 9.8, the bioavailability of Pb in soils and other contaminated media varies greatly. Numerous risk assessments have shown soil and dust Pb to be major factors for Pb exposure by children. Often the remediation strategy used for Pb-contaminated soils in residential areas (see Chapter 12) is excavation and replacement with clean soil. Research is also under way in an attempt to find ways to reduce Pb bioavailability with soil amendments *in situ* so that excavation is not needed. The IEUBK model can be used to assess the effects of the reductions in Pb bioavailability.

For contaminated sites the goal of remediation is often to have less than 5% of the children with greater than 10 $\mu\text{g}/\text{dL}$ blood Pb concentration. Figure 13.6 shows the blood Pb concentration ranges for a number of situations. Situation 1 has 800 mg Pb/kg soil with 30% absolute bioavailability, which estimates 17.5% of the children 6 to 72 months old would have >10 $\mu\text{g}/\text{dL}$ blood Pb concentration. Default values were used for all remaining input variables. Situations 2 and 3 produce similar results in that approximately 5% of the children exceed 10 $\mu\text{g}/\text{dL}$ blood Pb concentration. Situation 2 used the model to determine the soil Pb concentration that would give the desired blood Pb distribution. In this case a soil Pb concentration of 375 mg/kg reduced the percentage of children exceeding 10 $\mu\text{g}/\text{dL}$ from 17.5 to 5%. If this were a community with Pb-contaminated soil, the results suggest that soil with a Pb concentration exceeding 375 mg/kg should be removed. Situation 3 uses 800 mg/kg soil Pb again, but reduces the absolute bioavailability to 15% (a 50% reduction). Here, similar results are obtained as compared with situation 2, but the implications are that an *in situ* remediation would be able to accomplish the same goal. An *in situ*

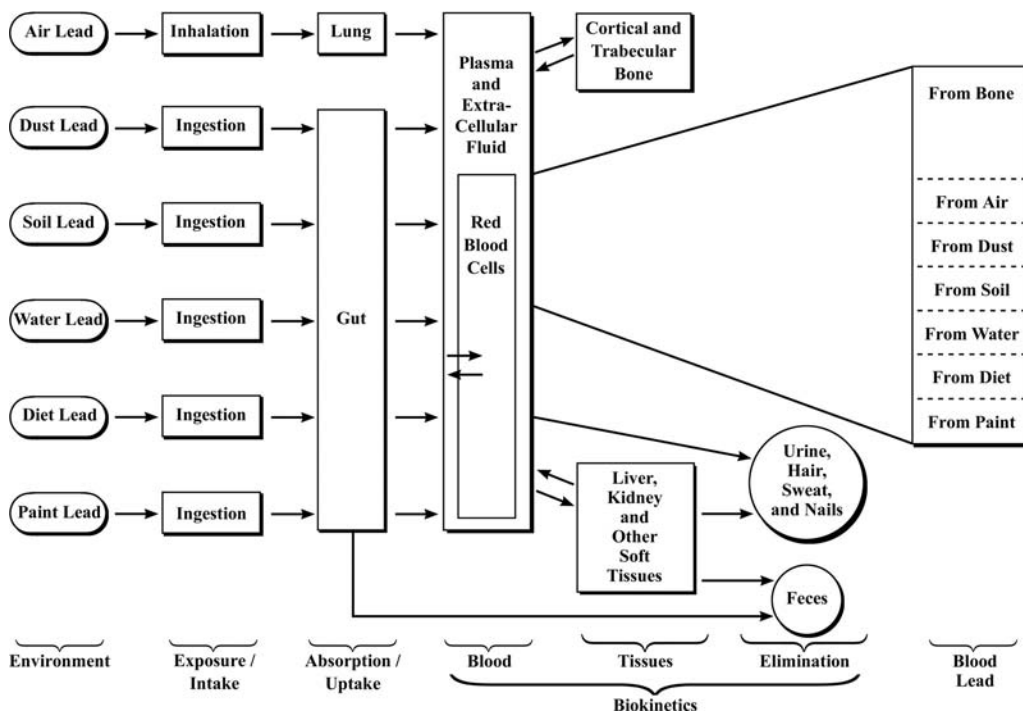


Figure 13.5 Schematic of the IEUBK model. (From U.S. EPA, 1994.)

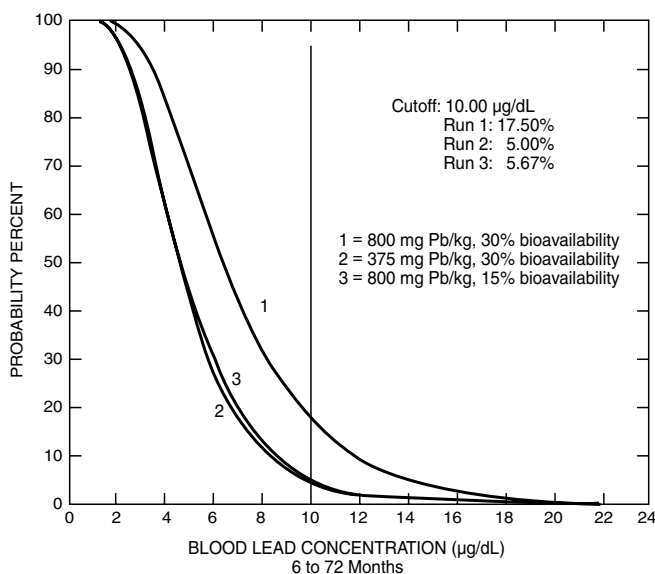


Figure 13.6 IEUBK model output showing the influence of soil Pb bioavailability on the proportion of children 6 to 72 months of age who have >10 µg/dL blood Pb concentration. Curve 1 assumes 800 mg Pb/kg soil and 30% bioavailability while curve 3 uses 800 mg Pb/kg and 15% bioavailability. Curve 2 uses 30% bioavailability and shows that soil Pb cannot exceed 375 mg/kg to have no more than 5% of the children with >10 µg/dL blood Pb concentration.

remediation would have tremendous cost advantages and would be less disruptive than soil excavation, but people would have to accept that the Pb was still present, but not in a harmful form.

PROBLEMS

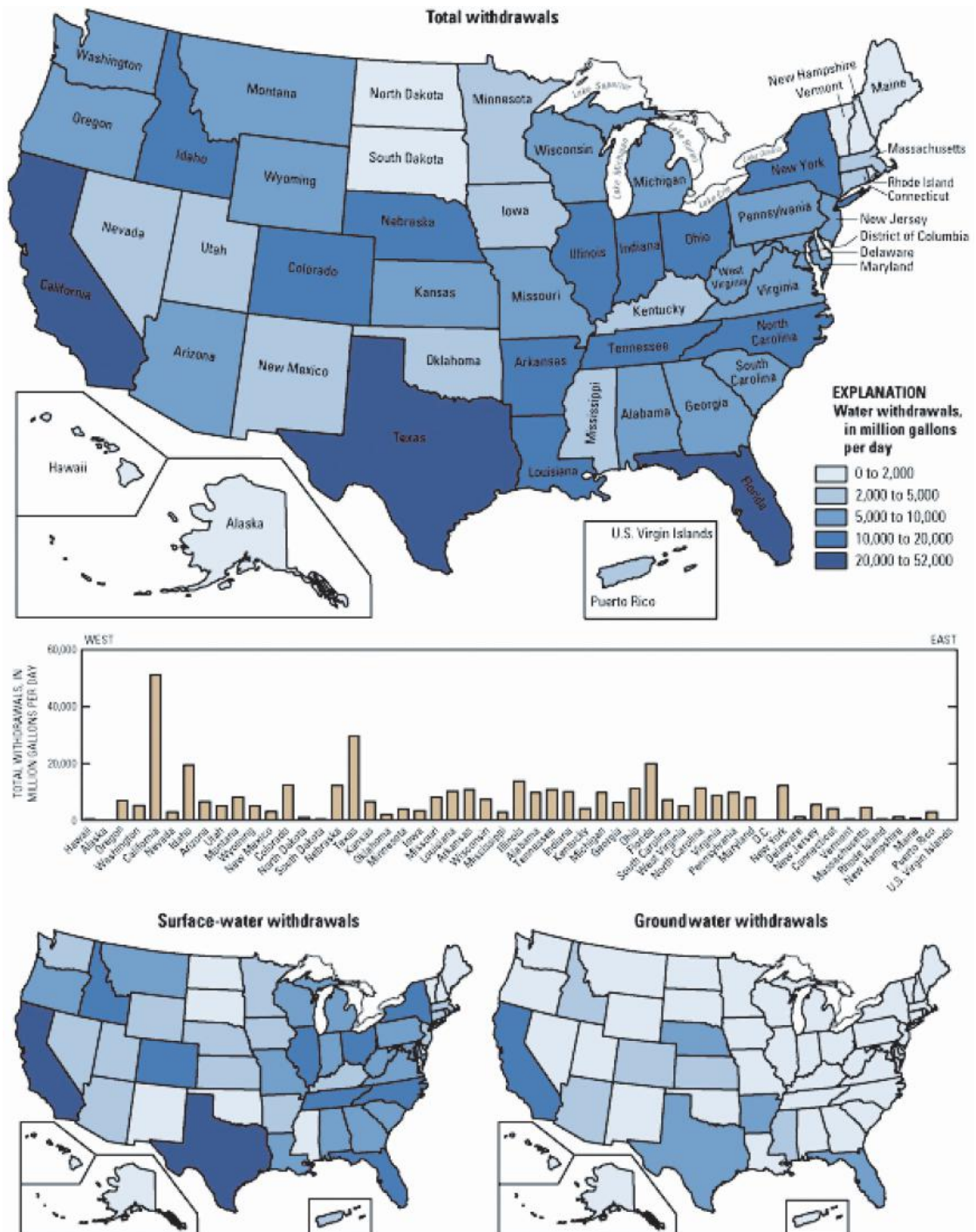
- 13.1 There is a clear difference in actual risks vs. how those risks are perceived by the general public and politicians. What are some of the advantages and disadvantages of this discrepancy? Should regulatory agencies actively work at educating people about this difference so that the public's perception of risk corresponds to actual risks?
- 13.2 Consider a nuclear reactor meltdown, an automobile accident, the crash of a commercial airliner, and the release of genetically engineered organisms into the environment. Rank the risk of death from each according to the perceived risk by the general public. Estimate the actual risk of death from each and compare the ranking to that for risk perception.
- 13.3 Using the Example Problem 13.1 equations (pp. 486 and 487) recalculate the MCLG for atrazine in drinking water assuming (a) the lowest NOAEL value found in animal studies was 1.0 mg/kg/day; (b) a safety factor of 10 was used to calculate the RfD instead of a factor of 100; and (c) that 80% of the atrazine a person receives is from drinking water.
- 13.4 Describe how the determination of the MCL for atrazine in drinking water would be affected if atrazine were a Category I substance instead of a Category II substance.
- 13.5 Describe the differences between an absolute risk standard and a negligible risk standard. Discuss the advantages and disadvantages of each.
- 13.6 Perform unit analysis on the Example Problem 13.2 equation (p. 487) and demonstrate that the units for RP are kg/ha.
- 13.7 Recalculate RP from Example Problem 13.2 assuming that RE = 0.5 instead of 1.0 and comment on the difference. How does this calculation relate to the concept of bioavailability?
- 13.8 Discuss the differences and similarities between human health risk assessment and ecological risk assessment.

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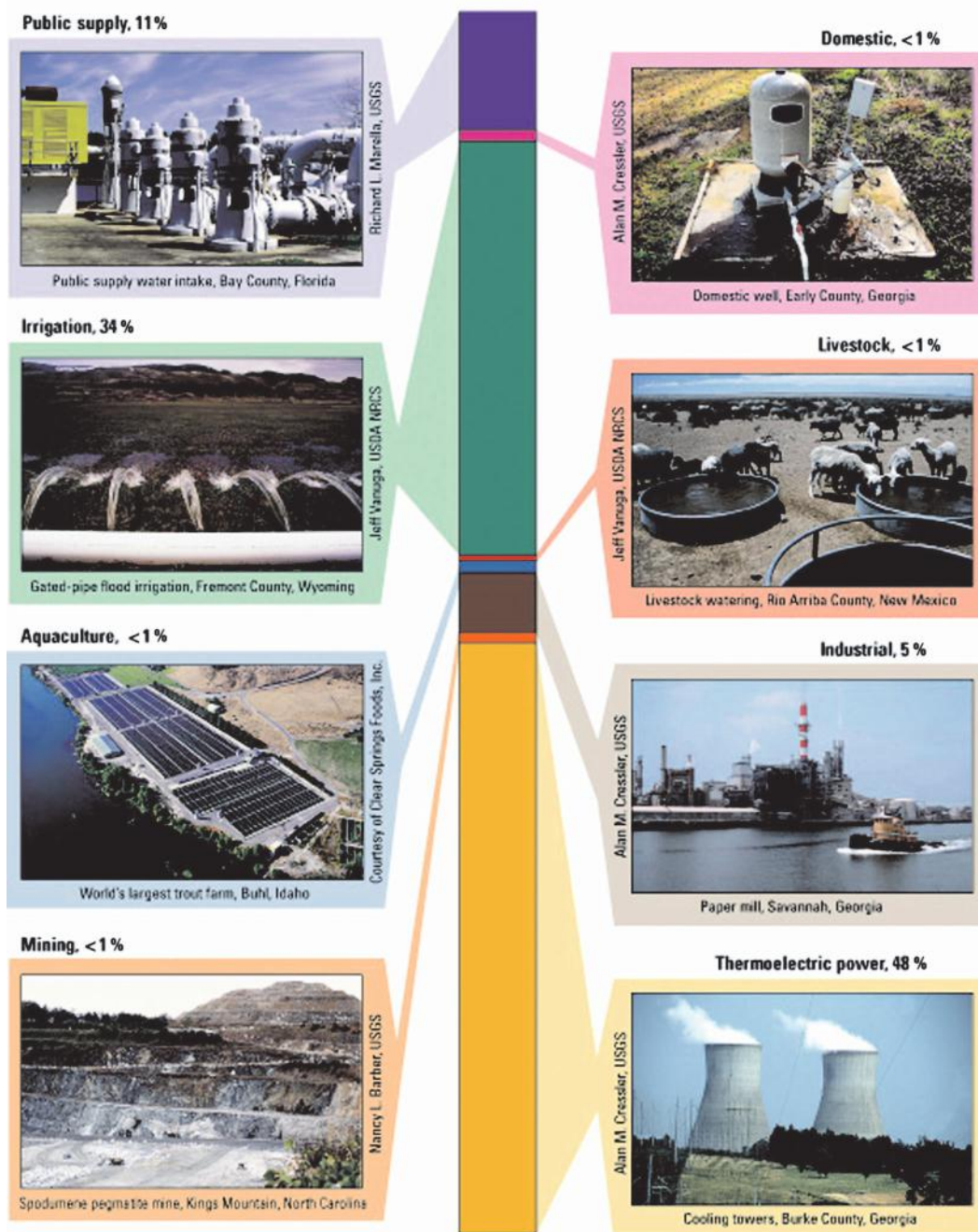
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SUPPLEMENTARY MATERIALS

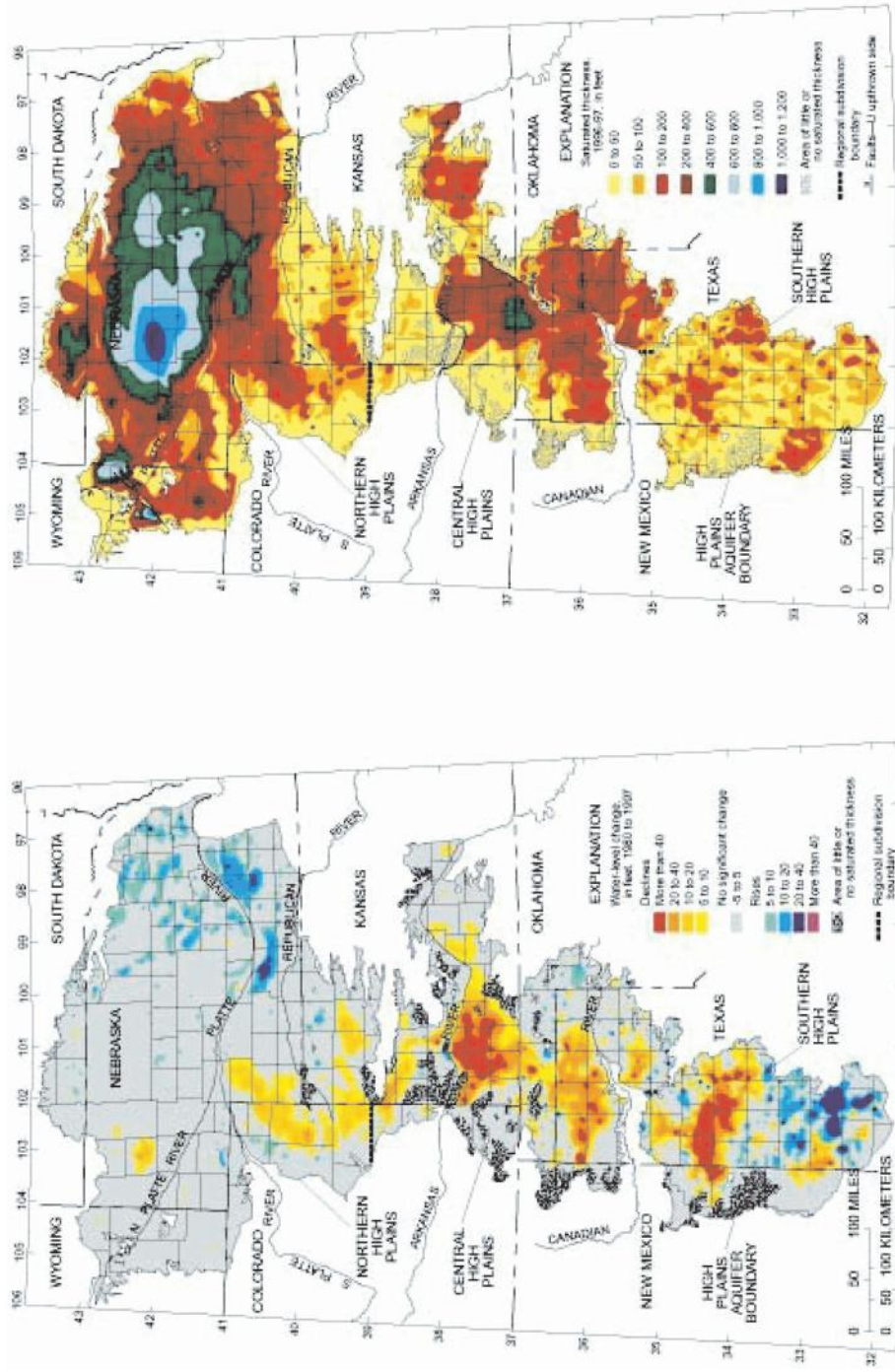
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Color Figure 2.13 Geographic distribution of total, surface water, and groundwater withdrawals in the United States during 2000. Note that California, Texas, and Florida accounted for 25% of total water withdrawals. California and Texas utilize 17% of the total surface-water withdrawals, whereas California alone accounts for 18% of the total groundwater withdrawals. (From Hutson, S. S. et al., Estimated Use of Water in the United States in 2000, U.S. Geological Survey. USGS Circular 1268, released March 2004, revised April 2004, May 2004.)

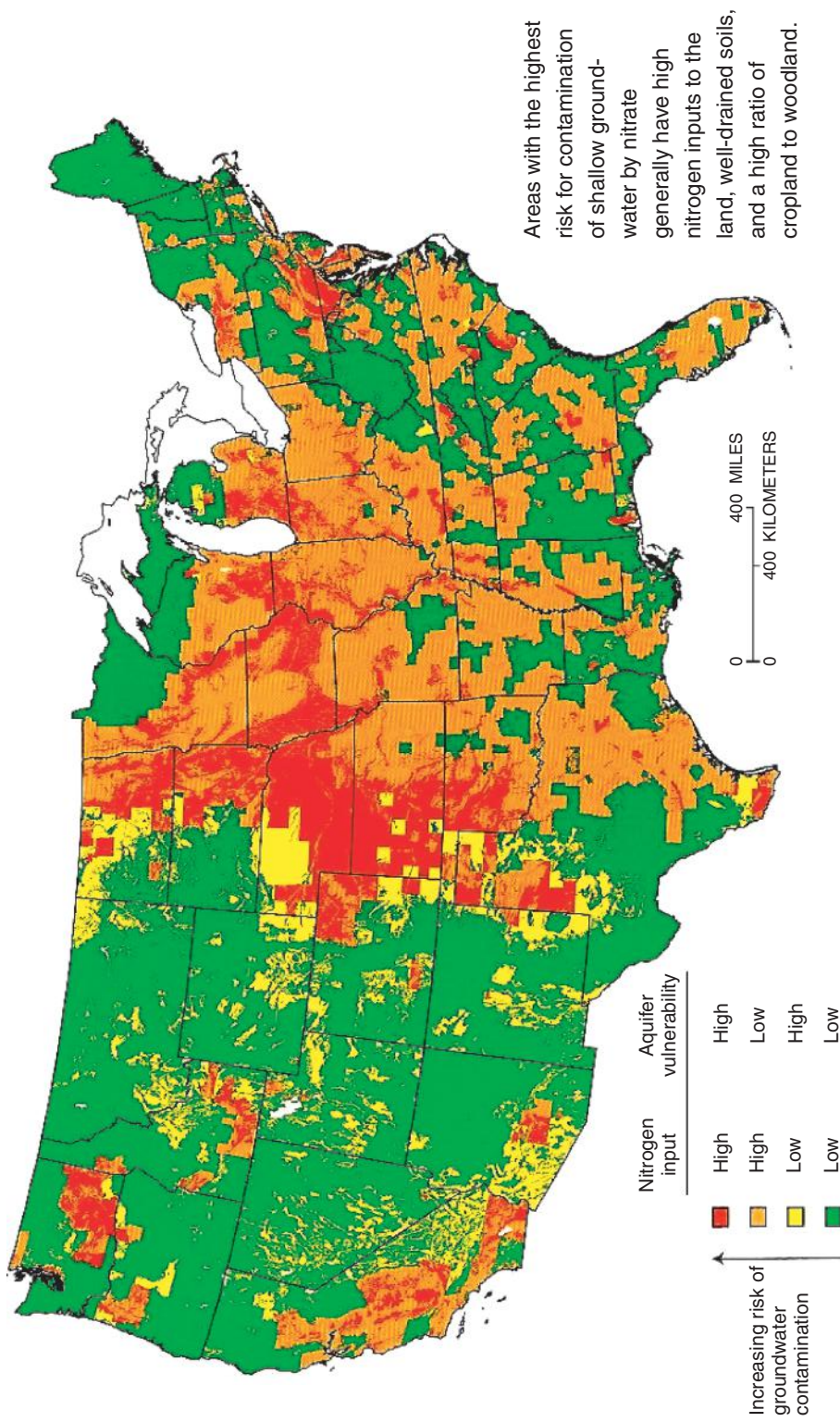


Color Figure 2.14 Water use in the United States for 2000 based on estimates of water withdrawals for public supply, domestic, irrigation, livestock, aquaculture, industrial, mining, and thermoelectric power. (From Hutson, S. S. et al., Estimated Use of Water in the United States in 2000, U.S. Geological Survey. USGS Circular 1268, released March 2004, revised April 2004, May 2004.)

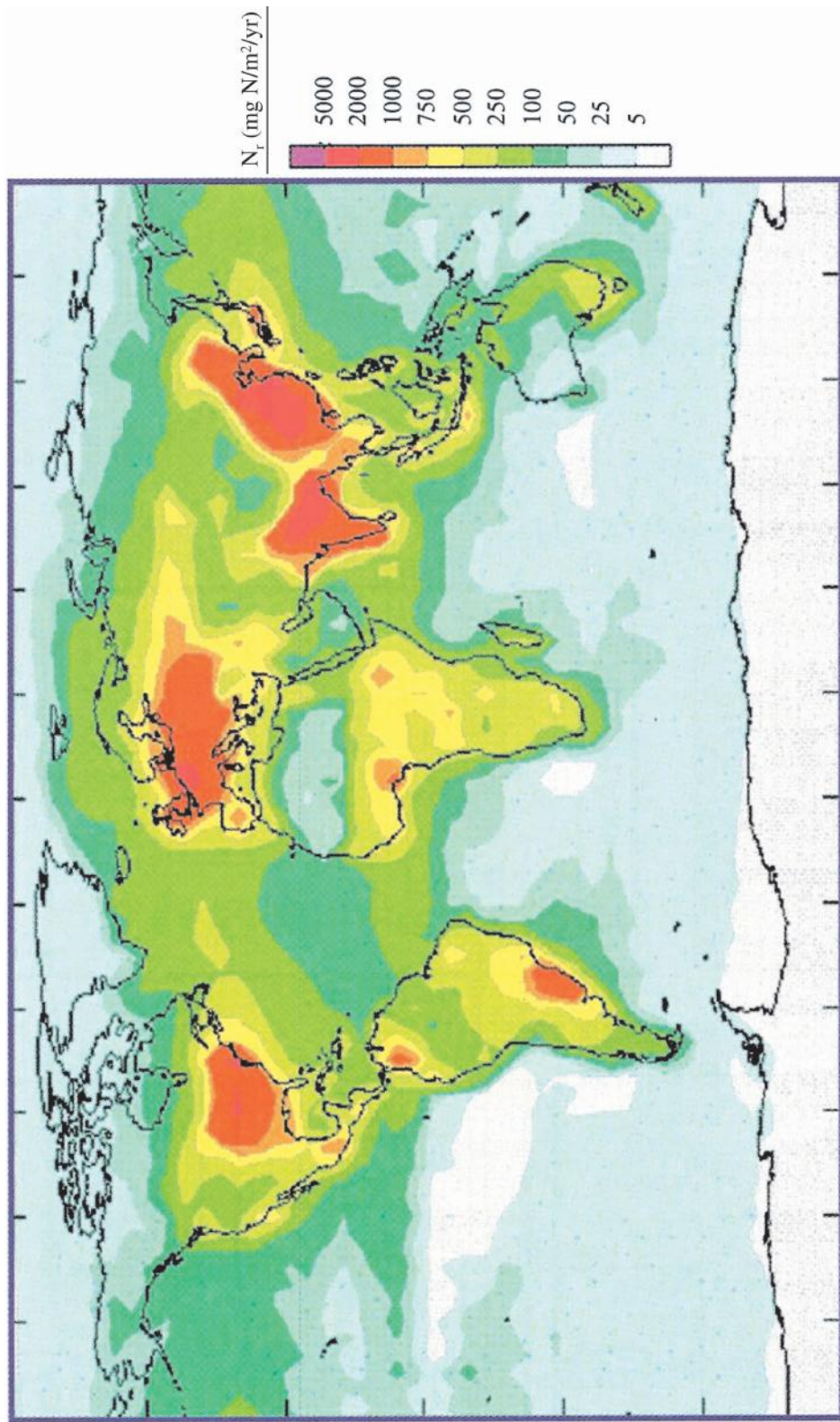


Color Figure 2.16

Water level change (1980 to 1997) and saturated thickness (vertical distance between the water table and the aquifer floor) of the Ogallala Aquifer in 1996–1997. Note that the aquifer is depleted in parts of northern Texas and west central Kansas, and that a large portion of the Ogallala water exists beneath the Nebraska Sandhills, which remains relatively untapped due to a lack of crop irrigation that is deemed uneconomical. (From McGuire, V. L. et al., Water-level changes, 1980 to 1997, in the high plains aquifer, U.S. Geological Survey Fact Sheet FS-124-99, Washington, D.C. Available at http://ne.water.usgs.gov/highplains/hp97_web_report/fs-124-99.htm.)



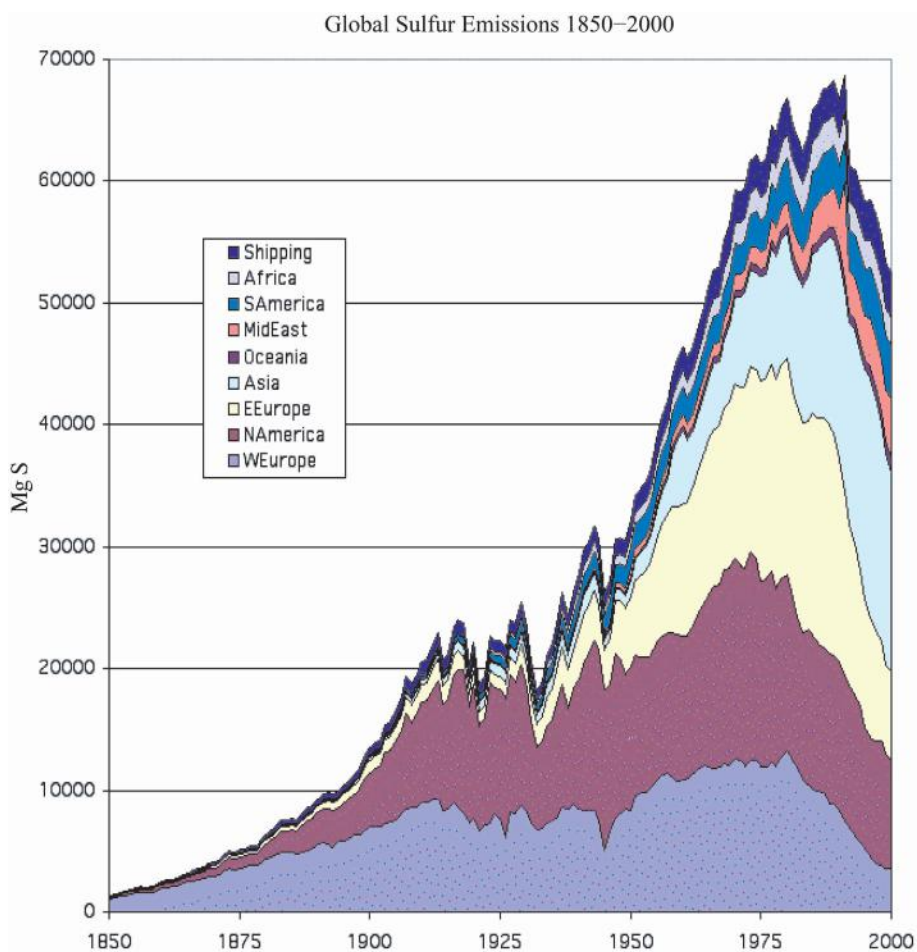
Color Figure 5.4 Geographic nature of the estimated risk of $\text{NO}_3\text{-N}$ contamination of groundwater in the United States based on a USGS model integrating nitrogen inputs and aquifer vulnerability. (From USGS, 1999.)



Color Figure 5.7 Global deposition of reactive nitrogen (N_r) on the Earth's continents and oceans in 1993. (From Galloway, J. N. and E. B. Cowling, *Ambio*, 31, 64–71, 2002. With permission.)



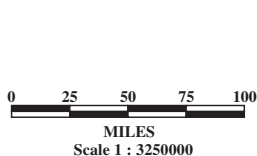
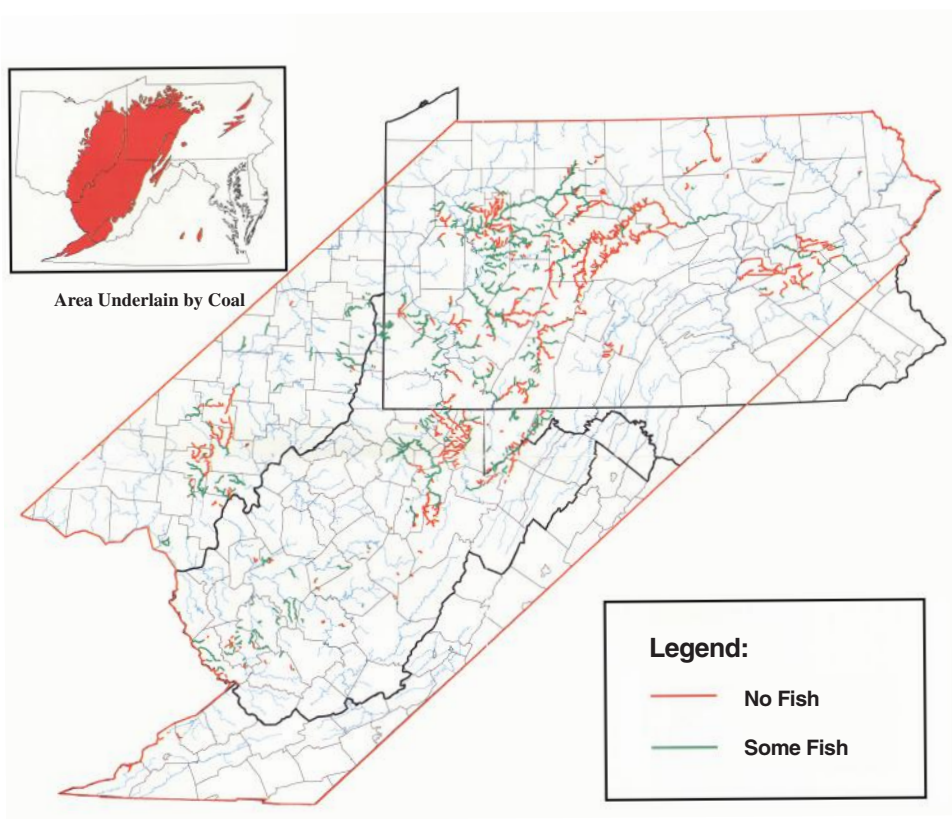
Color Figure 6.1 Eutrophic canal next to a pasture in the Netherlands.



Color Figure 7.1 Global sulfur emissions. Note the dramatic decline in emissions in the 1990s. (From David Stern's Web site <http://www.rpi.edu/~sternd/datasite.html>. With permission.)

Streams with Fisheries Impacted by Acid Mine Drainage in MD, OH, PA, VA, WV

(Based on EPA Fisheries Survey — 1995)

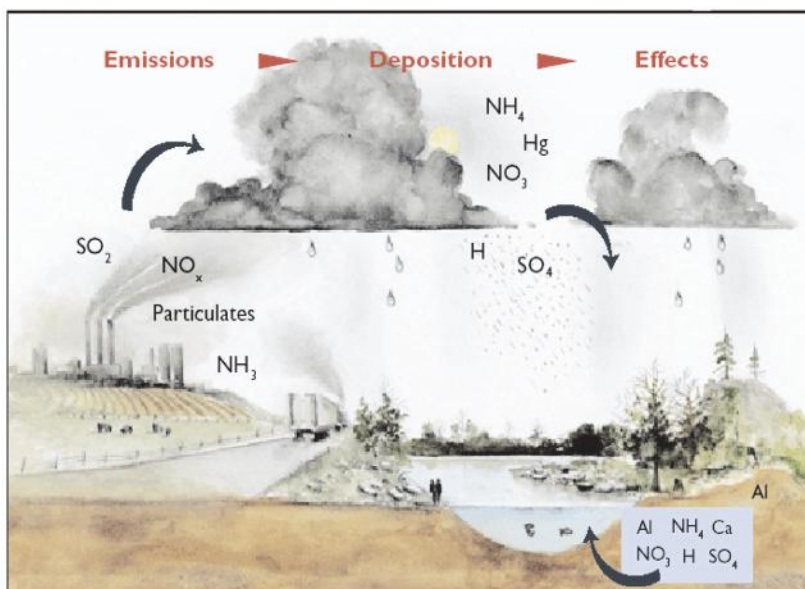


Stream Miles Impacted			
State	No Fish	Some Fish	Total
OH	258	349	607
PA	1714	1525	3239
WV	488	612	1100
VA	17	0	17
MD	42	110	152
TOTAL	2519	2596	5115

Color Figure 7.12 Fish habitats affected by AMD within Maryland, Ohio, Pennsylvania, Virginia, and West Virginia. (From U.S. EPA, 1995.)



Color Figure 10.10 Phytoremediation. Native vegetation growing on the Phytoremediation/Greenbelt located within the Union Pacific Railroad (UPRR) Tie Plant, Laramie, Wyoming. The Laramie Greenbelt was opened to the public in 2001 and includes a park, bike path, and walkway that run approximately five miles along the Laramie River. A portion of the UPRR Tie Plant received a topsoil cover over the surface soils to prevent any exposure of the remaining low-level soil contamination. Although the site is considered protective of human health and the environment, continued monitoring of both the phytoremediation (use of plants) sites and the potential risks to wildlife will be conducted under RCRA by the Wyoming Department of Environmental Quality every 5 years.



Color Figure 11.12 Acid deposition. Acidic deposition is a complex problem that has primarily originated from burning of fossil fuels. Although it was regarded as a simple problem that was limited in scope when first identified some 40 years ago, scientists now know that acids and acidifying compounds can move through terrestrial, biological, and surface water environments, resulting in a series of adverse ecological effects. (From Driscoll, C. T. et al. 2001. Acid rain revisited: advances in scientific understanding since the passage of the 1970 and 1990 Clean Air Act Amendments, Hubbard Brook Research Foundation, *Sci. Links Publ.*, 1, 1, 2001. Available at http://www.hubbardbrook.org/hbrf/publications/Acid_Rain_Revisited.pdf. With permission.)

Appendix

Table A.1 The Elements and Their Symbols, Atomic Numbers, and Atomic Weights Based on the Assigned Relative Atomic Mass of ¹²C = 12

Name	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227.028
Aluminum	Al	13	26.98154
Americium	Am	95	(243) ^a
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	(210)
Barium	Ba	56	137.33
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01218
Bismuth	Bi	83	208.9804
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Cesium	Cs	55	132.9054
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(254)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257)
Fluorine	F	9	18.998403

continued

Table A.1 The Elements and Their Symbols, Atomic Numbers, and Atomic Weights Based on the Assigned Relative Atomic Mass of $^{12}\text{C} = 12$ (continued)

Name	Symbol	Atomic Number	Atomic Weight
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.9665
Hafnium	Hf	72	178.49
Helium	He	2	4.00260
Holmium	Ho	67	164.9304
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.9045
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.967 ± 0.003
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.9380
Mendelevium	Md	101	(257)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.179
Neptunium	Np	93	237.0482
Nickel	Ni	28	58.70
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97376
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.9077

continued

Table A.1 The Elements and Their Symbols, Atomic Numbers, and Atomic Weights Based on the Assigned Relative Atomic Mass of $^{12}\text{C} = 12$ (continued)

Name	Symbol	Atomic Number	Atomic Weight
Proactinium	Pa	91	231.0359
Promethium	Pm	61	(145)
Radium	Ra	88	226.0254
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.868
Sodium	Na	11	22.98977
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.9479
Technetium	Tc	43	(97)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.9254
Thallium	Tl	81	204.37
Thorium	Th	90	232.0381
Thulium	Tm	69	168.9342
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.9415
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

^a Anthropogenic element or one that occurs only in minute quantities in nature.

Table A.2 Conversion Factors for SI and Non-SI Units

To Convert Column 1 into Column 2, Multiply by	Column 1 SI Unit	Column 2 Non-SI Unit	To Convert Column 2 into Column 1, Multiply by
Length			
0.621	kilometer, km (10 ³ m)	mile, mi	1.609
1.094	meter, m	yard, yd	0.914
3.28	meter, m	foot, ft	0.304
1.0	micrometer, μm (10 ⁻⁶ m)	micron, μ	1.0
3.94 × 10 ⁻²	millimeter, mm (10 ⁻³ m)	inch, in.	25.4
10	nanometer, nm (10 ⁻⁹ m)	Angstrom, Å	0.1
Area			
2.47	hectare, ha	acre	0.405
247	square kilometer, km ² (10 ³ m) ²	acre	4.05 × 10 ⁻³
0.386	square kilometer, km ² (10 ³ m) ²	square mile, mi ²	2.590
2.47 × 10 ⁻⁴	square meter, m ²	acere	4.05 × 10 ³
10.76	square meter, m ²	square foot, ft ²	9.29 × 10 ⁻²
1.55 × 10 ⁻³	square millimeter, mm ² (10 ⁻³ m) ²	square inch, in ²	645
Volume			
9.73 × 10 ⁻³	cubic meter, m ³	acre-inch	102.8
35.3	cubic meter, m ³	cubic foot, ft ³	2.83 × 10 ⁻²
6.10 × 10 ⁴	cubic meter, m ³	cubic inch, in ³	1.64 × 10 ⁻⁵
2.84 × 10 ⁻²	liter, L (10 ⁻³ m ³)	bushel, bu	35.24
1.057	liter, L (10 ⁻³ m ³)	quart (liquid), qt	0.946
3.53 × 10 ⁻²	liter, L (10 ⁻³ m ³)	cubic foot, ft ³	28.3
0.265	liter, L (10 ⁻³ m ³)	gallon	3.78

33.78	liter, L (10^{-3} m ³)	ounce (fluid), oz	2.96×10^{-2}
2.11	liter, L (10^{-3} m ³)	pint (fluid), pt	0.473
Mass			
2.20×10^{-3}	gram, g (10^{-3} kg)	pound, lb	454
3.52×10^{-2}	gram, g (10^{-3} kg)	ounce (avdp), oz	28.4
2.205	kilogram, kg	pound, lb	0.454
0.01	kilogram, kg	quintal (metric), q	100
1.10×10^{-3}	kilogram, kg	ton (2000 lb), ton	907
1.102	megagram, Mg (tonne)	ton (U.S.), ton	0.907
1.102	tonne, t	ton (U.S.), ton	0.907
Yield and Rate			
0.893	kilogram per hectare, kg/ha	pound per acre, lb/acre	1.12
7.77×10^{-2}	kilogram per cubic meter, kg/m ³	pound per bushel, lb/bu	12.87
1.49×10^{-2}	kilogram per hectare, kg/ha	bushel per acre, 60 lb	67.19
1.59×10^{-2}	kilogram per hectare, kg/ha	bushel per acre, 56 lb	62.71
1.86×10^{-2}	kilogram per hectare, kg/ha	bushel per acre, 48 lb	53.75
0.107	liter per hectare, L/ha	gallon per acre	9.35
893	tonnes per hectare, t/ha	pound per acre, lb/acre	1.12×10^{-3}
893	megagram per hectare, Mg/ha	pound per acre, lb/acre	1.12×10^{-3}
0.446	megagram per hectare, Mg/ha	ton (2000 lb) per acre, ton/acre	2.24
2.24	meter per second, m/s	mile per hour, mi/h	0.447
Specific Surface			
10	square meter per kilogram, m ² /kg	square centimeter per gram, cm ² /g	0.1
1.000	square meter per kilogram, m ² /kg	square millimeter per gram, mm ² /g	0.001

continued

Table A.2 Conversion Factors for SI and Non-SI Units (continued)

To Convert Column 1 into Column 2, Multiply by	Column 1 SI Unit	Column 2 Non-SI Unit	To Convert Column 2 into Column 1, Multiply by
Pressure			
9.90	megapascal, MPa (10 ⁶ Pa)	atmosphere	0.101
10	megapascal, MPa (10 ⁶ Pa)	bar	0.1
1.00	megagram per cubic meter, Mg/m ³	gram per cubic centimeter, g/cm ³	1.00
2.09 × 10 ⁻²	pascal, Pa	pound per square foot, lb/ft ²	47.9
1.45 × 10 ⁻⁴	pascal, Pa	pound per square inch, lb/in ²	6.90 × 10 ³
Temperature			
1.00 (K - 273)	Kelvin, K	Celsius, °C	1.00 (°C + 273)
(9/5 °C) + 32	Celsius, °C	Fahrenheit, °F	5/9 (°F - 32)
Energy, Work, Quantity of Heat			
9.52 × 10 ⁻⁴	joule, J	British thermal unit, Btu	1.05 × 10 ³
0.239	joule, J	calorie, cal	4.19
10 ⁷	joule, J	erg	10 ⁻⁷
0.735	joule, J	foot-pound	1.36
2.387 × 10 ⁻⁵	joule per square meter, J/m ²	calorie per square centimeter (langley)	4.19 × 10 ⁴
10 ⁵	newton, N	dyne	10 ⁻⁵
1.43 × 10 ⁻³	watt per square meter, W/m ²	calorie per square centimeter minute (irradiance), cal/cm ² min	698
Transpiration and Photosynthesis			
3.60 × 10 ⁻²	milligram per square meter second, mg/m ² s	gram per square decimeter hour, g/dm ² h	27.8

5.56 × 10 ⁻³	milligram (H ₂ O) per square meter second, mg/m ² s	micromole (H ₂ O) per square centimeter second, μmol/cm ² s	180
10 ⁻⁴	milligram per square meter second, mg/m ² s	milligram per square centimeter second, mg/cm ² s	10 ⁴
35.97	milligram per square meter second, mg/m ² s	milligram per square decimeter hour, mg/dm ² h	2.78 × 10 ⁻²
Plane Angle			
57.3	radian, rad	degrees (angle), °	1.75 × 10 ⁻²
Electrical Conductivity, Electricity, and Magnetism			
10	siemen per meter, S/m	millimho per centimeter, mmho/cm	0.1
10 ⁴	tesla, T	gauss, G	10 ⁻⁴
Water Measurement			
9.73 × 10 ⁻³	cubic meter, m ³	acre-inches, acre-in.	102.8
9.81 × 10 ⁻³	cubic meter per hour, m ³ /h	cubic feet per second, ft ³ /s	101.9
4.40	cubic meter per hour, m ³ /h	U.S. gallons per minute, gal/min	0.227
8.11	hectare-meters, ha-m	acre-feet, acre-ft	0.123
97.28	hectare-meters, ha-m	acre-inches, acre-in.	1.03 × 10 ⁻²
8.1 × 10 ⁻²	hectare-centimeters, ha-cm	acre-feet, acre-ft	12.33
Concentrations			
1	centimole per kilogram, cmol/kg (ion-exchange capacity)	milliequivalents per 100 grams, meq/100 g	1
0.1	gram per kilogram, g/kg	percent, %	10
1	milligram per kilogram, mg/kg	parts per million, ppm	1

continued

Table A.2 Conversion Factors for SI and Non-SI Units (continued)

To Convert Column 1 into Column 2, Multiply by	Column 1 SI Unit	Radioactivity	Column 2 Non-SI Unit	To Convert Column 2 into Column 1, Multiply by
2.7×10^{-1} 2.7×10^{-2} 100 100	becquerel, Bq	Radioactivity	curie, Ci	3.7×10^{10}
	becquerel per kilogram, Bq/kg		picocurie per gram, pCi/g	37
	gray, Gy (absorbed dose)		rad, rd	0.01
	sievert, Sv (equivalent dose)		rem (roentgen equivalent man)	0.01
Plant Nutrient Conversion				
	Elemental		Oxide	
2.29	P		P ₂ O ₃	0.437
1.20	K		K ₂ O	0.830
1.39	Ca		CaO	0.715
1.66	Mg		MgO	0.602

Source: American Society of Agronomy, Madison, WI. Reprinted with permission.

Table A.3 Journals and Periodicals Related to the Environmental Sciences

<i>ACTA Hydrochimica et Hydrobiologica</i>
<i>Advances in Soil Science</i>
<i>Aerosol Science and Technology</i>
<i>Agricultural Chemistry</i>
<i>Agricultural Ecosystems and Environment</i>
<i>Agrochimica</i>
<i>Agronomy Journal</i>
<i>AIHA Journal</i>
<i>Ambio</i>
<i>American Society of Agronomy Abstracts</i>
<i>Analyst</i>
<i>Analytical Chemica ACTA</i>
<i>Analytical Chemistry</i>
<i>Analytical Letters</i>
<i>Annali di Chimica</i>
<i>Annals of Agricultural and Environmental Medicine</i>
<i>Antarctic Science</i>
<i>Applied Catalysis A-General</i>
<i>Applied Soil Ecology</i>
<i>Aquatic Conservation—Marine and Freshwater Ecosystems</i>
<i>Archives of Environmental Contamination and Toxicology</i>
<i>Archives of Environmental Health</i>
<i>Arctic</i>
<i>Arctic Antarctic and Alpine Research</i>
<i>Arid Land Research and Management</i>
<i>Atmospheric Environment</i>
<i>Australian Journal of Soil Research</i>
<i>Biocycle</i>
<i>Biodiversity and Conservation</i>
<i>Biogeochemistry</i>
<i>Biological Conservation</i>
<i>Biology and Fertility of Soils</i>
<i>Biomedical and Environmental Sciences</i>
<i>Boreal Environment Research</i>
<i>Bulletin of Environmental Contamination and Toxicology</i>
<i>Canadian Journal of Chemistry</i>
<i>Canadian Journal of Fisheries and Aquatic Science</i>
<i>Canadian Journal of Soil Science</i>
<i>Catena</i>
<i>Chemical Speciation and Bioavailability</i>
<i>Chemosphere</i>

continued

Table A.3 Journals and Periodicals Related to the Environmental Sciences (*continued*)

<i>Clays and Clay Minerals</i>
<i>Climate Research</i>
<i>Climatic Change</i>
<i>Coastal Management</i>
<i>Communications in Soil Science and Plant Analysis</i>
<i>Compost Science and Utilization</i>
<i>Conservation Biology</i>
<i>CRC Critical Review of Environmental Contamination</i>
<i>Critical Reviews in Environmental Science and Technology</i>
<i>Crop Science</i>
<i>Ecological Economics</i>
<i>Ecological Engineering</i>
<i>Ecotoxicology</i>
<i>Ecotoxicology and Environmental Safety</i>
<i>Energy Policy</i>
<i>Environment</i>
<i>Environment International</i>
<i>Environment Management</i>
<i>Environmental and Ecological Statistics</i>
<i>Environmental and Experimental Botany</i>
<i>Environmental and Molecular Mutagenesis</i>
<i>Environmental Conservation</i>
<i>Environmental Engineering Science</i>
<i>Environmental Forensics</i>
<i>Environmental Geochemistry and Health</i>
<i>Environmental Geology</i>
<i>Environmental Geology and Water Science</i>
<i>Environmental Health Perspectives</i>
<i>Environmental Letters</i>
<i>Environmental Modeling & Assessment</i>
<i>Environmental Modeling and Software</i>
<i>Environmental Monitoring and Assessment</i>
<i>Environmental Pollution</i>
<i>Environmental Progress</i>
<i>Environmental Research</i>
<i>Environmental Science and Pollution Research</i>
<i>Environmental Science and Technology</i>
<i>Environmental Technology</i>
<i>Environmental Toxicology</i>
<i>Environmental Toxicology and Chemistry</i>
<i>Environmental Toxicology and Pharmacology</i>

continued

Table A.3 Journals and Periodicals Related to the Environmental Sciences (*continued*)*Environmetrics**Estuaries**Estuarine**Eurasian Soil Science**European Journal of Soil Biology**European Journal of Soil Science**Field Analytical Chemistry and Technology**Fresenius Environmental Bulletin**Gefahrstoffe Reinhaltung der Luft**Geochimica et Cosmochimica Acta**Geoderma**Geological Society of America Bulletin**Geomicrobiology Journal**Global Biogeochemical Cycles**Global Change Biology**Global Environmental Change**Global Environmental Change-Human and Policy Dimensions**Health Physics**Human and Ecological Risk Assessment**Industrial Health**International Biodeterioration and Biodegradation**International Journal of Biometeorology**International Journal of Environment and Pollution**International Journal of Environmental Analytical Chemistry**International Journal of Environmental Health Research**International Journal of Hydrogen Energy**International Journal of Life Cycle Assessment**Isotopes in Environmental and Health Studies**Journal of Aerosol Science**Journal of Agricultural and Environmental Ethics**Journal of Arid Environments**Journal of Atmospheric Chemistry**Journal of Chemical Ecology**Journal of Chemical Education**Journal of Coastal Research**Journal of Contaminant Hydrology**Journal of Environmental Biology**Journal of Environmental Engineering-ASCE**Journal of Environmental Health**Journal of Environmental Management**Journal of Environmental Monitoring**continued*

Table A.3 Journals and Periodicals Related to the Environmental Sciences (continued)

<i>Journal of Environmental Quality</i>
<i>Journal of Environmental Radioactivity</i>
<i>Journal of Environmental Science and Health Part A–Toxic/Hazardous Substances & Environmental Engineering</i>
<i>Journal of Environmental Science and Health Part B–Pesticides Food Contaminants and Agricultural Wastes</i>
<i>Journal of Environmental Science and Health Part C–Environmental Carcinogenesis & Ecotoxicology Reviews</i>
<i>Journal of Environmental Science Technology</i>
<i>Journal of Environmental Sciences–China</i>
<i>Journal of Environmental Toxicology and Contamination</i>
<i>Journal of Exposure Analysis and Environmental Epidemiology</i>
<i>Journal of Great Lakes Research</i>
<i>Journal of Hazard Materials</i>
<i>Journal of Health Population and Nutrition</i>
<i>Journal of Hydrologic Engineering</i>
<i>Journal of Marine Research</i>
<i>Journal of Paleolimnology</i>
<i>Journal of Plant Nutrition and Soil Science–Zeitschrift für Pflanzenernährung und Bodenkunde</i>
<i>Journal of Soil & Water Conservation</i>
<i>Journal of the Air & Waste Management Association</i>
<i>Journal of the Air Pollution Control Association</i>
<i>Journal of the American Water Works Association</i>
<i>Journal of the Association of Official Analytical Chemists</i>
<i>Journal of the Chartered Institution of Water and Environmental Management</i>
<i>Journal of the Geological Society (London)</i>
<i>Journal of the Indian Chemical Society</i>
<i>Journal of the Water Pollution Control Federation</i>
<i>Journal of Toxicology and Environmental Health</i>
<i>Land Degradation & Development</i>
<i>Limnology and Oceanography</i>
<i>Marine Chemistry</i>
<i>Marine Environmental Chemistry</i>
<i>Marine Environmental Research</i>
<i>Marine Pollution Bulletin</i>
<i>Mountain Research and Development</i>
<i>Nature</i>
<i>Nutrient Cycling in Agroecosystems</i>
<i>Ozone–Science and Engineering</i>
<i>Physical Geography</i>
<i>Plant and Soil</i>
<i>Polar Research</i>

continued

Table A.3 Journals and Periodicals Related to the Environmental Sciences (*continued*)

Polish Journal of Environmental Studies
Radiation and Environmental Biophysics
Radiation Protection Dosimetry
Regulated Rivers—Research & Management
Remote Sensing of Environment
Resources Conservation and Recycling
Reviews of Environmental Contamination and Toxicology
River Research and Applications
SAR and QSAR in Environmental Research
Science
Science of the Total Environment
Soil and Crop Science Society of Florida Proceedings
Soil and Sediment Contamination
Soil and Tillage Research
Soil Biology and Biochemistry
Soil Science
Soil Science and Plant Nutrition
Soil Science Society of America Journal
Soil Use and Management
Stochastic Environmental Research and Risk Assessment
Talanta
Vadose Zone Journal
Waste Management
Waste Management & Research
Water Air and Soil Pollution
Water Environment Research
Water Research
Water Resources Research
Water Science and Technology
Weed Science Journal
Wetlands

Table A.4 Decision Case Studies in the *Journal of Natural Resources and Life Sciences Education* (1998–present) That May Be Useful in Courses in the Environmental Sciences

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Table A.5 Prefixes Used in the SI System of Units

Prefix	Symbol	Order of Magnitude
yocto	y	10^{-24}
zepto	z	10^{-21}
atto	a	10^{-18}
femto	f	10^{-15}
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
deka	da	10^1
hecto	h	10^2
kilo	k	10^3
mega	M	10^6
giga	G	10^9
tera	T	10^{12}
peta	P	10^{15}
Exa	E	10^{18}
zetta	Z	10^{21}
yotta	Y	10^{24}

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